# MOBILITY OF DIOXINS AND FURANS FROM STABILIZED INCINERATION RESIDUE IN SEAWATER

BY

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## Abstract of the Thesis

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Residues from several municipal solid waste incinerator facilities were analyzed for dioxin and furan concentrations. Levels within fly ash samples ranged between no detection (ND) - 1250 ng/g of ash and ND - 450 ng/g for total PCDD's and PCDF's, respectively. Levels within combined ash samples ranged between ND - 60 ng/g and ND - 17 ng/g for PCDD's and PCDF's, repectively.

Mobilization of dioxins and furans from raw incinerator ash and stabilized incinerator ash was investigated in seawater and distilled water using tank leachate and sequential batch extraction techniques. No dioxins or furans were detected in any leachate or water extract.

The data from this study suggests that dioxins and furans associated with incinerator residues are not readily released from raw ash or stabilized ash into seawater or distilled water.

# DEDICATION

To the Creator of the Earth and oceans,

with thankfulness and praise.

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# INTRODUCTION

Long Island, New York is in the process of stopping the landfilling of municipal solid waste (MSW) to protect the Island's groundwater supply. This action, ordered by the New York State Legislature, has created a new problem in refuse management. Local governments are being forced to find alternative MSW disposal practices that are environmentally sound and economically feasible. Many communities are choosing incineration as an alternative to landfilling; however, substantial controversy arises from this choice due in part to the residues produced by an operating facility (Steisel *et al.*, 1987). Leachate from incinerator residues in landfills has the potential to pollute groundwater, making landfilling of these products unacceptable. The ash from the incineration process normally contains significant amounts of metals including lead, cadmium, zinc, copper, manganese, silver, mercury, and tin (Roethel *et al.*, 1986). Other contaminants include organic compounds such as polychlorinated biphenyls (PCB's), polychlorinated dioxins and furans (PCDD's and PCDF's), polycyclic aromatic hydrocarbons (PAH's), chlorophenols, and chlorobenzenes (Sawell and Constable, 1988b). These contaminants have been found in the residue streams, bottom ash, wash waters, fly ash, and chimney stack discharges of solid waste incinerators. The total amount of these compounds formed varies from day to day and varies among incinerators depending on operating conditions, type of plant, and refuse composition. Since incineration is being chosen as an alternative to landfilling, environmentally sound ash management strategies need to be developed.

Initial studies have shown that stabilization of incinerator residues, using Portland type V cement, produces solid block forms that may be environmentally acceptable (Roethel *et al.*, 1986). Physical and chemical properties and the strength of these stabilized incineration ash (SIA) blocks have been tested to investigate the possibility of using such blocks for construction, including underwater construction in the sea. Roethel *et al.* (1986) have performed seawater dissolution studies on SIA blocks to determine the leaching kinetics of inorganic constituents of environmental concern. Their investigation has confirmed that stabilization considerably reduces the release of metals from incinerator residues. However, the fate of organic contaminants, such as dioxins and furans, has not yet been investigated. It is the goal of this study to assess the impact presented by dioxins and furans in the use of SIA blocks in aquatic environments.

# OBJECTIVES

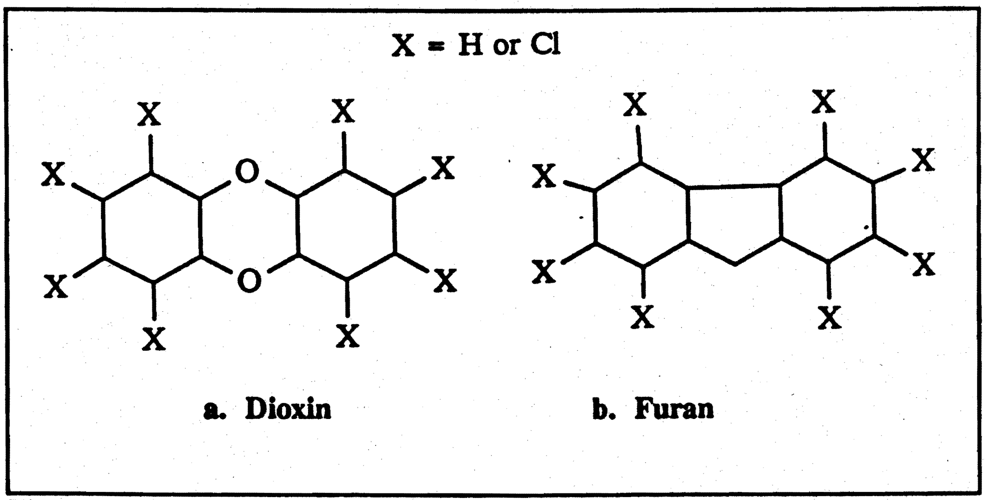
The overall objective of this study is to explore the mobility of dioxins and furans from stabilized incinerator ash (SIA) in aquatic environments and to assess the potential environmental impact posed by the dioxins and furans present. The specific objectives of this research are:

1. To develop the analytical protocols necessary to detect very low levels of chlorinated dioxins and furans in both solid and liquid samples.
2. To measure total concentrations of chlorinated dioxins and furans in selected municipal solid waste incinerator ash samples.
3. To investigate the mobility of dioxins and furans in incinerator ash, stabilized incinerator ash, and stabilized incinerator ash proctor blocks using leaching experiments and sequential batch extraction techniques.
4. To conclude from the results of these experiments whether stabilization of incinerator ash immobilizes dioxins and furans, making the material suitable for use in aquatic environments.

# BACKGROUND

## Chemical Structure

Polychlorinated dibenzo-*p*-dioxins (PCDD's), commonly known as dioxins, are a group of tricyclic, planar, aromatic compounds. The common name refers to the basic structure of two oxygen atoms linking two benzene rings (Fig. 1a). Chlorine atoms can be substituted for the hydrogen atoms on the rings, producing the chlorinated dioxins, of which there are 75 isomers. These compounds are generally inert to acids, bases, reduction, and at temperatures <200°C, oxidation and heat (ATSDR, 1989). Chemical



a. Dioxin

b. Furan

**Figure 1. Basic chemical structure of dioxin and furan.**

**Table I. List of dioxin and furan homolog groups and isomers.**

| Number of Cl | Homolog Abbreviations | Number of Isomers CDD | CDF |
|---|---|---|---|
| 1-Mono | MCDD(F) | 2 | 4 |
| 2-Di | DCDD(F) | 10 | 16 |
| 3-Tri | TriCDD(F) | 14 | 28 |
| 4-Tetra | TCDD(F) | 22 | 38 |
| 5-Penta | PeCDD(F) | 14 | 28 |
| 6-Hexa | HxCDD(F) | 10 | 16 |
| 7-Hepta | HpCDD(F) | 2 | 4 |
| 8-Octa | OCDD(F) | 1 | 1 |
| Poly | PCDD(F) | 75 | 135 |

inertness tends to increase with increasing chlorination. Polychlorinated dibenzofurans (PCDF's) are similar in structure to the dioxins, but having onlyone oxygen atom between the two benzene rings (Fig. 1b). Chlorine atom substitutions can produce 135 chlorinated furan isomers. Table I lists the possible homolog groups and number of isomers in each group for dioxins and furans.

## Formation

Dioxins and furans are widely distributed in the environment. Many studies have shown the presence of PCDD's and PCDF's in soil samples, water samples, air particulates and total air samples as well as in sediments from lakes, rivers and marine environments (Hutzinger and Fiedler, 1989; Meyer *et al.*, 1989; Rappe *et al.*, 1988; Tiernan *et al.*, 1989). These compounds are released by gasoline- and diesel-fueled truck and car exhausts, residential fireplaces and grills, and cigarettes (Bingham *et al.*, 1989; Bumb et al., 1980). Dioxins and furans are not intentionally manufactured except as reference standards for research. However, many of these compounds occur as impurities from the manufacture of industrial and agricultural chemicals based on chlorophenols and certain chlorinated aromatic hydrocarbons. They are also formed by the burning of scrap plywood and mill wastes that are treated with chlorophenols as fungicides. The burning provides sufficient heat to convert the chlorophenols into dioxins or phenoxyphenols (dioxin precursors). There is even some evidence that commonly used chlorophenols and chlorinated biphenyls are converted to dioxins by sunlight (Miller and Zepp, 1987). Other sources of dioxins and furans are the combustion of biosludge from pulp mills (Mantydoski *et al.*, 1989), emissions from scrap metal melting processes (Tysklind *et al.*, 1989), and municipal waste incinerators. It is also known that dioxins and furans are present in paper mill discharges (Chiu *et al.*, 1989; Clement *et al.*, 1989). The greatest concentrations are found in the effluents and particulates from bleached kraft mills, where the tetrachlorinated dioxins and furans are the predominant congeners. Clement *et al.*, (1989) found concentrations ranging from 190 to 680 parts-per-trillion (pptr) TCDD and 430 to 6300 pptr for TCDF. No TCDD was detected in non-bleached-kraft mills, semi-bleached-kraft mills, and bleached-kraft-sulfite mills. Isomer specific analyses are now available that can identify the industrial source of contamination.

The pattern of isomers and congeners found in environmental samples is treated like a fingerprint, as each source typically produces only a distinctive configuration (Rappe *et al*, 1987; Stalling *et al.*, 1986).

## Toxicology

Dioxins and furans are considered environmental pollutants due to the extreme biological potency and potential chronic effects of certain isomers (Amdur *et al.*, 1991). However, toxicologists are unable to agree on the significance of exposure to trace quantities of these compounds. Animal studies and *in vitro* experiments have indicated that there is a difference in toxic and biological effects among the different isomers. Toxicities can vary by a factor of 1000 to 10,000 for closely related isomers as shown in Table II, in which 2,3,7,8-TCDD is assigned a relative toxicity factor of one. The 2,3,7,8-TCDD toxic equivalencies presented in Table II are those used by the United States Environmental Protection Agency (US EPA) throughout this study in estimating risks of exposure to dioxin and furan mixtures (Bellin and Barnes, 1987). It should be noted that the US EPA method has been modified recently (North Atlantic Treaty Organization, 1988). The isomers with the highest activity and acute toxicity are those having 4-6 chlorine atoms with all lateral positions (2,3,7,and 8) substituted with chlorine (Rappe, 1984). If one or more of the chlorine atoms are removed or placed in other positions, or if the molecule is changed so that it is no longer planar, toxicity decreases.

The biochemistry of these compounds is not fully understood and is a subject of active research. In general, it has been proposed that 2,3,7,8-TCDD acts through a receptor-mediated mechanism. The TCDD binds with the Ah (aromatic hydrocarbon) receptor from the cytoplasm or nucleus of a cell, exerts its action in the nucleus by interacting with DNA, and triggers a pleiotropic response (Poland and Glover, 1976; Roberts *et al.*, 1985; WHO, 1989). Some scientists believe that several thousand receptors have to be affected before any biological response can be seen (Roberts, 1991). If this

**Table II. EPA-recommended toxic equivalency factors for dioxins and furans.**

| Compound | Toxic Equivalency Factors |
|---|---|
| Mono through Trichlorodibenzo-*p*-dioxins | 0 |
| 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin | 1 |
| Other Tetrachlorodibenzo-*p*-dioxins | 0.01 |
| 2,3,7,8-substituted Pentachlorodibenzo-*p*-dioxins | 0.5 |
| Other Pentachlorodibenzo-*p*-dioxins | 0.005 |
| 2,3,7,8-substituted Hexachlorodibenzo-*p*-dioxins | 0.04 |
| Other Hexachlorodibenzo-*p*-dioxins | 0.0004 |
| 2,3,7,8-substituted Heptachlorodibenzo-*p*-dioxins | 0.001 |
| Other Heptachlorodibenzo-*p*-dioxins | 0.00001 |
| Octachlorodibenzo-*p*-dioxin | 0 |
| 2,3,7,8-Tetrachlorodibenzofuran | 0.1 |
| Other Tetrachlorodibenzofurans | 0.001 |
| 2,3,7,8-substituted Pentachlorodibenzofurans | 0.1 |
| Other Pentachlorodibenzofurans | 0.001 |
| 2,3,7,8-substituted Hexachlorodibenzofurans | 0.01 |
| Other Hexachlorodibenzofurans | 0.0001 |
| 2,3,7,8-substituted Heptachlorodibenzofurans | 0.001 |
| Other Heptachlorodibenzofurans | 0.00001 |
| Octachlorodibenzofuran | 0 |

theory is correct, a threshold level should exist for dioxins and furans, below which no toxicity will occur.

Animal studies using specific isomers of dioxins have demonstrated that toxic and biological effects are dependent on factors such as species, age and sex of the animal (ATSDR, 1989; Kimbrough, 1990; WHO, 1989). Toxic effects observed include body weight loss, birth defects, cancer, skin disorders, liver and thymus damage, gastric lesions, porphyria, suppression of the immune system, and death from undefined causes. Other biological effects include altered serum enzyme concentrations, induction of microsomal enzymes, and Vitamin A depletion (ATSDR, 1989; WHO, 1989). Thymic atrophy is a sensitive index of TCDD exposure in many animals. Chloracne, on the other hand, is the most prominent symptom for human exposure. Toxicological studies with humans are inconclusive. Occupational exposures and industrial accidents have caused chloracne and possibly minor functional disorders (Fingerhut *et al.*, 1991; Kimbrough, 1990; WHO, 1989).

The 2,3,7,8-TCDD isomer is extremely toxic in low doses, although different animal species vary widely in their sensitivity (Poland and Knutson, 1982). Although some isomers are more potent than others, the effects are the same for all isomers once the threshold level is reached. Since there is a large variation in toxicity and biological potency among isomers, risk evaluation of incinerator ash and leachates should be based on the levels of the more potent isomers. It is for this reason that 2,3,7,8-substituted isomers are distinguished from the other isomers in this study whenever possible, and 2,3,7,8-TCDD toxic equivalencies are calculated. Tetra- through octa-chlorinated dioxins and furans are monitored in this study. Mono- through tri-chlorinated compounds were not monitored due to the extremely low toxicity and zero 2,3,7,8-TCDD toxic equivalency factor of these compounds.

## Physical and Chemical Properties

There are certain processes and several physical chemical properties of dioxins that are important when predicting their fate in the environment and particularly in aquatic systems. The properties include water solubility, vapor pressure, Henry's law constant, octanol-water partition coefficient, and soil-water partition coefficient. Unfortunately, the physical chemical property data on dioxins are not extensive, may vary by an order of magnitude, and in some cases are contradictory. Care has been taken in selecting physical chemical property data for this report. References are always given to allow readers to make their own judgements.

Dioxins are highly lipophilic and have a very low water solubility. In general, as the number of chlorine atoms increases, solubility decreases (Shiu *et al.*, 1988). Solubility measurements vary among investigators and methods used for the determination. It has also been suggested that adsorption of the compounds to colloidal particles in the water used for determination often result in false solubility measurements. Table III lists several solubility measurements for selected dioxin congeners.

2,3,7,8-TCDD begins to degrade at 500°C, and for the most part, all 2,3,7,8-TCDD will be decomposed at 800°C within 21 seconds (ATSDR, 1989). Vapor pressures are very low at room temperatures, generally

**Table III. Aqueous solubilities of selected chlorinated dibenzo-*p*-dioxins at 25° C.**

| Compound | Solubility µg/l | Reference |
|---|---|---|
| dibenzo-*p*-dioxin | 842-900 | Shui *et al.*, 1988 |
| 1-chlorodibenzo-*p*-dioxin | 417 | Shui *et al.*, 1988 |
| 2,3-dichlorodibenzo-*p*-dioxin | 14.9 | Shui *et al.*, 1988 |
| 1,2,4-trichlorodibenzo-*p*-dioxin | 8.41 | Shui *et al.*, 1988 |
| 1,2,3,4-tetrachlorodibenzo-*p*-dioxin | 0.47-0.63 | Shui *et al.*, 1988 |
| 2,3,7,8-tetrachlorodibenzo-*p*-dioxin | 0.2 | Friesen *et al.*, 1973 |
|  | 0.00791 | Adams and Blaine, 1986 |
|  | 0.0193 | Marple *et al.*,1986 |
| 1,2,3,4,7-pentachlorodibenzo-*p*-dioxin | 0.118• | Friesen *et al.*, 1973 |
| 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin | 0.00442• | Friesen *et al.*, 1973 |
| 1,2,3,4,6,7,8-heptachloro-dibenzo-*p*-dioxin | 0.0024• | Friesen *et al.*, 1973 |
| octachlorodibenzo-*p*-dioxin | 0.0004 | Friesen *et al.*, 1973 |

• measured at 20 °C.

decreasing with increasing chlorination (Shiu *et al.*, 1988). The Henry's law constants range between 0.1 Pa-m$^3$/mol for a heptachlorinated dioxin to nearly 15 Pa-m$^3$/mol for a monochlorinated dioxin. These values correspond to dimensionless air-water partition coefficients in the range of 4 x 10$^{-5}$ to 6 x 10$^{-3}$ respectively (Shiu *et al.*, 1988). However, the Henry's Law constant doubles with an increase in temperature of 16 °C at ambient conditions.

Therefore, temperature may play an important role in affecting the environmental fate of dioxins. Considering the above constants, volatilization of dioxins from aquatic systems may be slow, but under certain conditions could be significant. Nash and Beall (1980) demonstrated in field and environmental chamber studies that TCDD is volatile. Their data show that vaporized TCDD can be found in the air at very low levels even though the evaporation rate is very low. Schroy *et al.* (1985) determined that TCDD is volatile at ambient temperatures (30-71 °C), and the vapor behaves as an ideal gas in that temperature range.

The octanol-water partition coefficients, expressed log $K_{ow}$, range from 4.3 to 8.2 with the value for 2,3,7,8-TCDD at 6.8 (Shiu *et al.*, 1988). Table IV lists octanol-water partition coefficients for selected dioxins and furans. When the solubility of a chemical in octanol is similar to the solubility in lipids, $K_{ow}$ can be used to estimate bioaccumulation and sorption to organic carbon. Recent studies on aquatic macrophytes have shown that the octanol-water partition coefficient imitates the plant-water bioconcentration factor for hydrophobic organic substances up to log $K_{ow}$ of 8.3 (Gobas *et al.*, 1991). In this case, these substances have a higher solubility in the plant lipids than in the water, basically making bioconcentration a thermodynamically controlled process.

**Table IV. Octanol-water partition coefficients for selected chlorinated dibenzo-*p*-dioxins and dibenzofurans at 25°C.**

| Compound | Log $K_{ow}$ | Reference |
|---|---|---|
| dibenzo-*p*-dioxin | 4.37 | Shiu *et al.*, 1988 |
| | 4.2 | Burkhard and Kuehl, 1986 |
| 2-chlorodibenzo-*p*-dioxin | 4.94 | Shiu *et al.*, 1988 |
| | 5.08 | Burkhard and Kuehl, 1986 |
| 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin | 7.02 | Burkhard and Kuehl, 1986 |
| | 6.42 | Sijm *et al.*, 1989 |
| | 6.64 | Marple *et al.*, 1986 |
| 1,2,3,7,8-pentachloro-dibenzo-*p*-dioxin | 6.64 | Sijm *et al.*, 1989 |
| 1,2,3,4,7-pentachloro-dibenzo-*p*-dioxin | 8.64-9.48 | Webster *et al.*, 1985 |
| | 7.40 | Shiu *et al.*, 1988 |
| 1,2,3,4,7,8-hexachloro-dibenzo-*p*-dioxin | 9.19-10.40 | Webster *et al.*, 1985 |
| | 7.80 | Shiu *et al.*, 1988 |
| 1,2,3,4,6,7,8-heptachlor-dibenzo-*p*-dioxin | 9.69-11.38 | Webster *et al.*, 1985 |
| | 8.00 | Shiu *et al.*, 1988 |
| octachlorodiobenzo-*p*-dioxin | 10.07-12.26 | Webster *et al.*, 1985 |
| | 8.20 | Shiu *et al.*, 1988 |
| 2,3,7,8-tetrachloro-dibenzofuran | 6.53 | Sijm *et al.*, 1989 |
| 2,3,4,7,8-pentachloro-dibenzofuran | 6.92 | Sijm *et al.*, 1989 |
| 1,2,3,4,6,7,8-heptachloro-dibenzofuran | 7.92 | Sijm *et al.*, 1989 |
| octachlorodibenzofuran | 7.97 | Doucette and Audren, 1988 |

Bioconcentration in fish tends to be similar; however recent studies have shown that the bioaccumulation factor-$K_{ow}$ relationship breaks down for more highly hydrophobic chemicals that exceed log $K_{ow}$ of 6.0 (Gobas *et al.*, 1989; Gobas *et al.*, 1991). Therefore, the $K_{ow}$ for a higher chlorinated dioxin is not accurate in estimating body burdens in fish and related aquatic organisms. They are still, however, important values since solubility and sorption processes usually correlate with this parameter (Opperhuizen 1986; Opperhuizen *et al.*, 1988).

Along with the solubility and octanol-water partition coefficient, the soil-water partition coefficient normalized to the organic carbon content of the sorbent ($K_{oc}$) is also an important environmental parameter. Walters and Guiseppi-Elie (1989) estimated the value of log $K_{oc}$ for TCDD at 6.6 by using log-linear extrapolation of $K_{oc}$ data obtained for the sorption of TCDD by soils from water/methanol mixtures. Walters *et al.* (1989) reported a log $K_{oc}$ value of 6.66 with water mixtures, agreeing well with the previous measurement.

## Fate in the Environment

One of the most important factors in assessing the hazards associated with contaminants such as dioxins and furans is their behavior in the environment. Environmental and health risks posed by substances that readily move by solubilization and/or volatilization can be quite different from risks posed by toxic materials that show little or no mobility. Dioxins generally reside in the soil and sediments. Since these organic compounds have a low solubility in water and volatility is relatively limited under most conditions, they eventually settle to the bottom and accumulate in the sediments of aquatic systems. Dioxins bind tightly to soil and sediment; this is important because it prevents rapid migration through soil and minimizes contamination of groundwater (Reggiani 1981).

A study done with octachlorodibenzo-*p*-dioxin (OCDD) in two separate five meter diameter by two meter deep lake mesocosms demonstrated that OCDD partitioned to particulate and dissolved organic matter and was removed from the water column with a half-life of 4 days (Servos *et al.*, 1989). Only one percent was determined to be dissolved in the water. Within 24 days, more than 98 percent of the OCDD added to the enclosures was found in the sediments. Most of the remaining two percent was in the water column sorbed to particulates and dissolved organic matter.

Many other studies have demonstrated the presence of PCDD's and PCDF's in the sediment of aquatic systems. Norwood *et al.* (1989) identified these compounds in estuarine sediments including sections of Eagle Harbor

(WA), New Bedford Harbor (MA), Narragansett Bay (RI), Black Rock Harbor (Bridgeport, CT), and Central Long Island Sound. Concentrations of dioxins were higher than furans for all samples except those from New Bedford Harbor which were more heavily contaminated with furans. The least contaminated sediment was collected from New Bedford Harbor, up-river from manufacturing facilities known to have released industrial wastewaters into the Harbor containing polychlorinated biphenyls. Isomer composition varied among estuarine systems suggesting different sources for these compounds.

Dioxins are environmentally stable and can persist for long periods when protected from light (Tschirley 1986). Processes that degrade these compounds in the environment are poorly understood, and additional study is needed. Under normal environmental conditions the only transformation process that is fairly rapid for dioxins is photolysis (Miller and Zepp, 1987; Miller *et al*, 1987). However, if the compounds are covered or settle beneath the surface of soils or water, half-lives may exceed ten years because of the protection from ultraviolet rays. Bopp *et al.* (1991) have found 2,3,7,8-TCDD and 2,3,7,8-TCDF to persist in anaerobic sediments of New Jersey estuaries on a time scale of several decades. During the photochemical decomposition process, higher chlorinated dioxins are dechlorinated in the presence of organic hydrogen donors (Rappe, 1984). Podoll *et al.* (1986) reported that the photolysis half-lives in surface waters varied from 21 hours in summer to 118 hours in winter.

Several microorganisms degrade dioxins, but at a very low rate (Tschirley, 1986). For example, a wood-decaying fungus, *Phanerochaete chryosporium*, is known to break down TCDD without observable toxicity to the organism (Bumpus *et al.*, 1985). This ability seems to be dependent on an extracellular lignin-degrading enzyme system (Miller and Zepp, 1987). In the sediments of aquatic systems, microbial degradation also occurs slowly, and the half-life of TCDD in this environment has been estimated to be one to three years (Reggiani, 1981). The six electron withdrawing atoms on the 2,3,7,8-TCDD molecule strongly inhibit oxidative metabolism, which partially explains why the rate of biodegradation is so low in aerobic environments.

Dioxins are not susceptible to hydrolysis at environmental temperatures (Podoll *et al.*,1986); therefore, this process is not environmentally significant. Chemical hydrolysis only occurs at extreme pH or temperatures or with catalysts not available in aquatic environments. Likewise, dioxins and furans lack active moieties and will not react easily with other compounds in normal environmental conditions.

Bioaccumulation is another important process to consider. It is likely that many of the same physical properties that result in strong binding to soil, such as extremely low water solubility and planar configuration, also result in high bioconcentration factors. Aquatic organisms have been found to be susceptible to the 2,3,7,8 isomers. Delayed chronic effects, such as reduced growth, fin necrosis, generalized edema, and degeneration of liver parenchymal cells, have been found in fish with short-term exposures to 2,3,7,8 isomers (O'Keefe *et al.*, 1983). 2,3,7,8-TCDD also has a relatively long half-life in fish, ranging from 58 days for juvenile rainbow trout to 109-317 days for coho salmon (Muir *et al.*, 1985). From these studies and those completed by Kuehl *et al.* (1985), it is known that 2,3,7,8 isomers readily bioaccumulate in fish. Kuehl *et al.* (1985) found that only the 2,3,7,8-TCDD accumulates in fish when the fish were exposed to TCDD's bound to fly ash or if the TCDD's were extracted by solvent extraction and spiked into the test water in a solvent free from the fly ash solid matrix. It has been suggested that this selectivity of 2,3,7,8-substituted isomers in fish is a result of the other isomers being more readily biodegraded or eliminated from the body.

To assess the magnitude of bioaccumulation, 2,3,7,8-TCDD concentrations in striped bass from the lower Hudson River were found to be 14-18 pptr (O'Keefe *et al.*, 1984). In the same study, striped bass from

Poughkeepsie, further up the Hudson River, had concentrations reaching 120 pptr. This is rather disturbing since striped bass, *Morone saxatilis*, is one of the most important commercial and recreational species along the Mid-Atlantic Coast of the United States. Harless *et al.* (1982) reported levels ranging from 4-695 pptr of 2,3,7,8-TCDD in the edible portion of various fishes from Saginaw Bay, Michigan. The highest concentrations were found in bottom-feeding catfish and carp. Servos *et al.* (1989) also observed the assimilation of dioxins in bottom-feeding fish. Studies by Batterman *et al.* (1989) indicated that bioaccumulation of 2,3,7,8-TCDD in fish occurs primarily through the food chain and secondarily through contact with contaminated sediment. It was also found that the amount of TCDD bioaccumulated from exposure to sediment samples was directly proportional to the sediment organic carbon TCDD concentrations. Exposure to water with low concentration of suspended solids did not seem to make a significant contribution to bioaccumulation. Many studies have been done on fish and other aquatic organisms from the Great Lakes, and the data indicate low background levels (1-300 pptr) of a series of dioxins and furans (Fehringer *et al.*, 1985; Rappe *et al.*, 1984; Ryan *et al.*, 1984). Other organisms such as snapping turtle from the Hudson River and Gray seal from the Baltic Sea were also found to contain several 2,3,7,8-PCDF isomers, with total furans reaching 3 ppb and 40 pptr respectively (Rappe *et al.*, 1984). Miyata *et al.* (1987) have found PCDDs in blue mussels and are using this organisms to monitor these compounds in coastal waters. Because of the high lipophilicity and long half-lives of 2,3,7,8-TCDD in organisms, human exposure through ingestion of fatty tissues of organisms that inhabit contaminated areas is anticipated to be significant.

It is interesting to note that in the majority of the aquatic organisms analyzed only the 2,3,7,8-substituted isomers are found. Crustaceans, however, contain other isomers. Norstrom *et al.* (1985) reported that crab hepatopancreas from the Canadian Pacific Coast contain 1,2,4,7,8-pentachlorodibenzo-*p*-dioxin, 1,2,3,6,7,9-hexachlorodibenzo-*p*-dioxin, and 1,2,3,6,8,9-hexachlorodibenzo-*p*-dioxin. Studies done on crabs and lobsters from the United States Atlantic Coast confirm this observation (Belton *et al.*, 1985). Invertebrates have also been found to readily accumulate 1,3,6,8-TCDD (Muir *et al.*, 1985). Reiersen and Iversen (1988) have reported crab claws contain 44 times the amount of TCDD found in the crab brown meat. Since invertebrates are capable of accumulating several different congeners and isomers, it may be possible to use them as signal organisms to detect the presence of environmental pollution of dioxins and furans.

With this in mind, it is important to determine how much of these compounds are available to the organisms in aquatic systems. Biota appear to be able to accumulate only the compound free in solution. Therefore, any complexation or sorption onto other surfaces will reduce the free concentration and the bioavailability of the dioxins (Karickhoff and Morris, 1987). It has been shown that both the apparent solubility and the bioavailability of dioxins are affected by particulate and dissolved organic matter (Webster *et al.*, 1986; Muir *et al.*, 1985; Servos and Muir, 1989; Kuehl *et al.*, 1985). Therefore, the concentration of dissolved organic matter in the water and sediments may greatly effect the fate of dioxins and their bioavailability. However, the source of dissolved organic matter can be even more important than the concentration. Servos and Muir (1989) found that 1,3,6,8-TCDD had a higher apparent solubility in simulated lake water than in purified, deionized water. They also found that the uptake rate constant for 1,3,6,8-TCDD in the amphipod, *Crangonyx laurentianus*, decreased as the dissolved organic carbon concentration increased. This might be due to increased dioxins in the bound phase as the dissolved organic carbon concentration increased, reducing bioavailability. This phenomenon has also been demonstrated by Kuehl *et al.* (1985) when carp exposed to fly ash with a high percentage organic carbon had lower 2,3,7,8-TCDD body residues than the carp exposed to fly ash with low percent organic carbon. This study also revealed that 2,3,7,8-TCDD can be tightly bound to carbon and is difficult to remove.

It is also important to consider that the sorption of dioxin to dissolved organic matter may even mobilize dioxins from soils or sediments that were thought to be permanent sinks for the compounds. This could result in wider dispersion of dioxins than otherwise expected. Since sorption is reversible (McCarthy and Jimenez, 1985), gradual desorption may be a source of freely dissolved dioxins in the water column producing continuous low-level exposures to aquatic organisms.

Since incinerator ash is most likely to reside in a landfill, it is important to consider groundwater transport as well. Murphy (1989) considered the leaching potential of 2,3,7,8-TCDD from ash in a landfill. Calculations were based on modified equations used by the U.S. EPA in its regulatory analyses, taking into account the physical and chemical characteristics of the compound. One of the models indicated that TCDD is virtually immobile in aquifer soils, requiring 9 million to 10 billion years to migrate 500 feet down-gradient of a landfill (Murphy, 1989).

To summarize their fate in the environment, dioxins and furans are basically transported while sorbed on particles, while dissolved in water, or while dispersed in the atmosphere. If photolysis is the primary pathway for degradation, transport to sunlight exposed areas may be the limiting factor for degradation in aquatic systems. The octanol-water partition coefficients and soil partition coefficients suggest that dioxins will be primarily adsorbed to particles in sediment and soil with very little in solution. These points are important to consider in assessing the potential hazards presented by dioxins and furans in the use of SIA blocks in aquatic environments.

## Techniques for Dioxin and Furan Analysis

The presence of dioxins and furans in the environment is not new. The reason for their recent attention is the development of new analytical techniques sensitive enough to detect these compounds at extremely low levels. Analyses needed to detect low levels of organic compounds are often complicated by the presence of other interfering substances such as polychlorinated biphenyls and other polychlorinated aromatics. These interfering compounds must be removed by chromatographic cleanup or instrumental techniques.

There are several types of analysis that may be used depending on the nature of the sample, the concentrations present, and the level of isomer specific trace detection required. Isomer specific analyses are very time consuming, involving much work. Therefore, it is helpful to use a relatively quick and simple method to detect the presence or absence of dioxins and furans in a sample before subjecting the sample to the elaborate cleanup needed for more detailed quantitation. Radioimmunoassay methods have been used for such a purpose (Karasek and Onuska, 1982). Individual dioxin isomers can not be identified with this technique.

Gas chromatography with electron capture detection (ECD/GC) can easily detect dioxins and furans at the 50 pg level (Karasek and Onuska, 1982). Retention times and response factors are used to quantify specific isomers. However, sample cleanup must be able to remove all interfering electron-capturing compounds. Therefore, only relatively simple samples or those that can be purified adequately can be analyzed by ECD/GC. High resolution gas chromatography with flame ionization has also been used (Tong and Karasek, 1986), producing isomer specific quantitation; although this technique is not as sensitive as electron capture detection.

High performance liquid chromatography (HPLC) is another technique used to analyze for dioxins (McGinnis *et al.*, 1979; Pfeiffer, 1976); however, it is more commonly used as a cleanup method. Nestrick *et al.* (1979) were able to separate all 22 TCDD isomers and to separate tetra- through octachlorinated congener groups (Lamparski and Nestrick, 1980). The fractionation combined reversed phase with normal phase (silica) HPLC. Each HPLC fraction collected contained groups of isomers that could be separated by gas chromatography and mass spectrometry.

Cleanup procedures using HPLC (Tong and Karasek, 1986) are advantageous due to rapid fractionation, ability to identify a wide range of compounds, and possible automation (Wagel *et al.*, 1980). HPLC techniques can be combined with other cleanup methods in isomer specific analyses of complex samples. Tong and Karasek (1986) have developed a technique to facilitate the use of gas chromatography with flame ionization and electron capture detection. These instruments are far less expensive than mass spectrometers and are more common in laboratories.

Gas chromatography and mass spectrometry (GC-MS) is the most widely used method of analysis and has a wide range of applicability when used in the selected ion monitoring mode. There are several GC-MS techniques available depending on GC resolution, method of MS ionization, mass resolution, or by tandem mass spectrometry (MS-MS). The most commonly used methods employ high resolution gas chromatography-low resolution mass spectrometry (HRGC-LRMS) and high resolution gas chromatography and high resolution mass spectrometry (HRGC-HRMS) with electron impact ionization. The most important variable in these techniques is the GC column used which depends on isomer specificity desired.

High resolution gas chromatography and low resolution mass spectrometry is used in this study. All dioxins and furans have strong, characteristic mass spectra and intense molecular ions (Karasek and Onuska, 1982) which allows this technique to clearly separate the individual dioxins and furans using reference standards and mass chromatograms. Typical detection limits are in the parts per billion (ppb) range. In order to detect part per trillion (pptr) levels in complex samples or 2,3,7,8-substituted isomers, high resolution gas chromatography is coupled with high resolution mass spectrometry. Samples are usually prepurified using multiple chromatographic cleanup techniques and/or HPLC as discussed earlier.

# MATERIALS

All solvents used in this research were Optima Grade or the highest available from Fisher Scientific, Pittsburgh, PA. Isotopically labeled PCDD and PCDF standards were purchased from Cambridge Isotope Laboratories, Woburn, MA, dissolved in either nonane or toluene. All standards were used as received without further purification. Working solutions were prepared by diluting with toluene. All standards and solutions were stored in the dark.

Materials used in the sample purification procedure were cleaned before use. All materials, excluding those in ovens, were stored in glass jars with teflon-lined screw caps. Both silica (Biosil A, 100-200 mesh, Bio-Rad Labs, Rockville Center, NY) and alumina (Basic Alumina AG-10, 100-200 mesh, Bio-Rad Labs) were precleaned by refluxing with toluene for 24 hours in a soxhlet apparatus. Silica was dried and activated in a vacuum oven at 130°C for at least three days prior to use. Alumina was dried and activated in a muffle furnace at 500°C for at least two days prior to use. Florisil, obtained from Fisher Scientific, was precleaned by refluxing with methylene chloride for 24 hours in a soxhlet apparatus, dried, and activated in oven at 130°C for at least 18 hours prior to use. Precleaning of Bondesil C-18 reverse-phase adsorbent (Analytichem International, Harbor City, CA) involved an acetone wash of 50g Bondesil per 1000 ml acetone followed by drying in a vacuum oven at 35 °C prior to use. Glasswool was precleaned by refluxing with toluene for 24 hours and air dried.

Basic-modified silica was prepared by combining 39g 1N sodium hydroxide and 100g precleaned, activated silica, and mixed thoroughly. Acid-modified silica was prepared similarly by combining 44g concentrated sulfuric acid and 100g precleaned, activated silica and mixed thoroughly. The carbon/celite mixture was prepared by combining 10.7g AX-21 Carbon (Anderson Development Co., Adrian, MI) and 124g Celite 545 (Fisher Scientific) and agitated to mix thoroughly.

Purified nitrogen gas used for evaporations was passed through a trap constructed of a copper tube containing coconut charcoal (Fisher Scientific) between glass wool plugs. A second trap filled with sodium sulfate was used to dry the nitrogen, followed by a microfiber filter to prevent migration of particles through the nitrogen line.

# METHODS

## Handling of Samples Containing Dioxins and Furans

The United States Environmental Protection Agency suggests that the handling of samples containing dioxins and furans should be done only by trained personnel who know and understand the appropriate procedures and the associated risks involved. Dioxin and furan standards and samples containing these compounds should handled by the same techniques as those used in the handling of radioactive or infectious materials. All laboratory waste items potentially contaminated with dioxins or furans during the analyses must be disposed of properly. For proper safety, handling, and disposal procedures, refer to EPA method 8280 (EPA, 1986).

## Ash Sample Collection

Most dioxins and furans found in municipal solid waste incinerator residue are formed after the combustion chamber when the gases are between 250-400°C (Hagenmaier *et al.*, 1987; Notrodt *et al.*, 1989; Stieglitz and Vogg, 1987; Vogg and Stieglitz, 1986). Reactions occur with oxygen, water, and hydrochloric acid in the presence of carbon particulates. Copper and other trace metals act as catalysts; chlorine sources in the solid waste stream may be plastic materials like polyvinylchloride and paper (Rappe *et al.*, 1987).

In this study dioxin and furan concentrations were determined in various ash samples including fly ash, bottom ash, and combined ash from different facilities during normal operating conditions. Fly ash, a very fine grained, low density ash, is composed of the particles suspended in the effluent gas. It is usually collected by electrostatic precipitators (ESP) that give the suspended ash an electrical charge and attract the charged particles to plates where they are trapped. Fly ash may also be collected by baghouses or fabric filters. Fly ash comprises approximately 15% of the total ash residue from a MSW incinerator and is usually mixed with bottom ash to form combined ash before prior to disposal. The particle size of fly ash typically ranges from less than one to several hundred microns. Bottom ash is the primary solid residue from an incinerator and is collected at the bottom grate after combustion. It is sorted by size of particles and passed near a magnet to remove ferrous materials for recycling. Aluminum may also be removed. For every ton of municipal solid waste burned, about one-quarter ton of residue is produced (Neal and Schubel, 1987).

The six facilities from which ash were obtained for this study were mass burn incinerators employing heat recovery located in the eastern United

States. Five of the six facilities are relatively new, placed in operation within the past five years. The exception is the incinerator in Glen Cove, Suffolk County, New York, which has been in operation since 1983. This incinerator burns 225 tons of MSW and 25 tons of sewage sludge (20% solids) per day. It has two refractory-wall furnaces with convection boilers. Particulates are controlled by an ESP but there is no control of acid gases. The second facility is located in Poughkeepsie, Dutchess County, New York and burns 400 tons per day (tpd) of MSW. The facility contains two rotary combustors; air pollution control consists of a dry scrubber and fabric filters for acid gas and particulate control.

Two of the facilities are located in New England and will be referred to as New England I and II. New England I is a 200 tpd plant which contains two water-walled boilers. Acid gases and particulates are contolled by a dry scrubber and fabric filters. New England II is a 1500 tpd facility that also contains two water-walled boilers. Air pollution control consists of a dry scrubber and an ESP for acid gas and particulate control. The last facility is located in Baltimore, Maryland, and it contains water-walled boilers. It is a 2250 tpd plant employing ESP for particulate control.

Composite samples of each ash type were collected during several hours of normal operation. This usually took place over a three day period.

Sampling occurred in both morning and afternoon sessions. Each composite sample from a particular session was mixed by spreading the material on a grid and randomly selecting grid sections to obtain representative samples for analysis. Ash samples were split into aliquots used to run duplicate analyses. Table V identifies the ash samples analyzed for PCDD/PCDF concentrations in this study.

Fly ash sample taken from New England I was subjected to further analyses to determine whether PCDD and PCDF were preferentially concentrated on the finer particles. The fly ash was passed through mesh screens resulting in three samples with particle size ranges of <45$\mu$m, 45-75$\mu$m, and 75-150$\mu$m. Particles >150$\mu$m were discarded. Each size fraction was analyzed separately using the same technique as used for the other ash samples.

## Stabilized Ash Preparation and Leaching Tank Configuration

Incineration residue from Baltimore was used to fabricate solid proctor-sized cylinders. The ash was combined with Portland Type V cement and water according to a previously determined optimum mix (Roethel *et al.*, 1986). A Soiltest Inc. proctor making machine was used to form the cylinders using a 5.5 pound rammer and 12 inch drop (ASTM Method No. D698, 1975).

**Table V. Identification of ash samples for PCDD and PCDF analysis.**

| Facility | Sampling Dates | Sample identification |
|---|---|---|
| Glen Cove, NY | 9/14/87 to 9/16/87 | 2 fly ash (GC-F-1, GC-F-2)<br>2 combined ash (GC-C-1, GC-C-2) |
| Dutchess County | 2/17/88 | 2 fly ash (1DC-F-1, 1DC-F-2)<br>2 combined ash (1DC-C-1, 1DC-C-2) |
| New England I | 4/11/88 to 4/13/88 | 2 fly ash (NEI-F-1, NEI-F-2)<br>1 combined ash (NEI-C)<br>1 bottom ash (NEI-B) |
| New England II | 9/13/88 to 9/15/88 | 1 fly ash (1NEII-F)<br>1 bottom ash (1NEII-B) |
| New England II | 11/19/88 to 11/21/88 | 1 fly ash (2NEII-F)<br>1 bottom ash (2NEII-B) |
| Dutchess County | 1/11/89 to 1/12/89 | 1 fly ash (2DC-F)<br>1 bottom ash (2DC-B) |
| Baltimore, MD | 8/8/89 to 8/11/89 | 1 combined ash (Balt-C) |

For comparison purposes, sand-gravel cement proctors were used as controls in leachate studies. Cement, sand, and gravel used in these processes were analyzed for dioxin and furan contamination prior to use.

After 28 days of curing at 25°C, the compressive strength of the proctors was tested and found to meet or exceed a strength of 1300 psi. Selected proctors were then submerged in glass tanks of distilled water or filtered seawater at a 4:1 liquid-to-solid ratio. Each tank was placed on a magnetic stirrer which kept the water constantly mixing at a slow speed. The top of each tank was covered with a glass plate from which the proctor was suspended by nylon string (Figure 2). This is similar to the set-up used by Roethel *et al.* (1986) for the leaching of calcium from SIA. The pH of each tank was monitored on a regular basis. Filtered seawater tanks were adjusted as required to pH 7.9 - 8.2 and distilled water tanks to pH 7.0 - 7.3 using dilute nitric acid. After ten months of submersion, the stabilized ash proctor and the sand-gravel proctor from both distilled water and filtered seawater tanks were removed, and the water from each of those four tanks was analyzed separately for dioxins and furans.

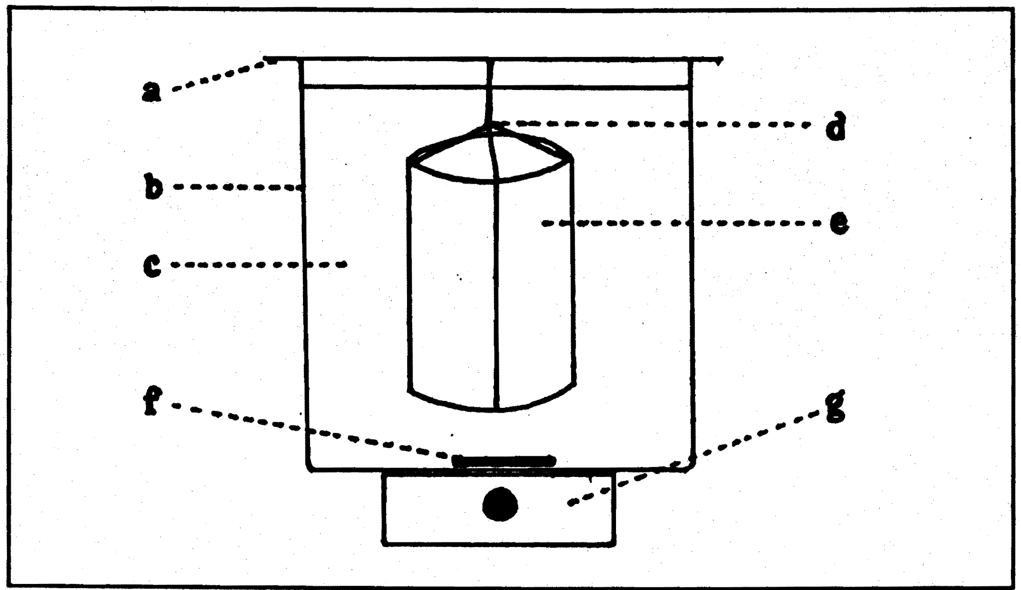


**Figure 2.** **Diagram of leaching tank configuration; a. glass cover;b. glass tank; c. water; d. nylon monofiliment string; e. stabilized incineration ash proctor block; f. magnetic stir bar; g. magnetic stirrer.**

**Table VI. Identification of leaching tank samples.**

| Proctor type | Water type |
|---|---|
| Stabilized Ash | filtered seawater |
| Stabilized Ash | distilled |
| Sand-gravel | filtered seawater |
| Sand-gravel | distilled |

## Sequential Batch Extraction

A sequential batch extraction procedure (ASTM Method No. D4793-88, 1982) was used to test the leachability of dioxins and furans from three different materials. Materials tested included Baltimore combined ash, Glen Cove fly ash, and crushed stabilized sand-gravel cement proctor. Each material was analyzed for dioxin and furan content. The sequential batch extraction procedure was carried out with both distilled water and filtered seawater for each type of material. Material was mixed with water at a 20:1 liquid-to-solid ratio for 18 hours. After mixing, the solid phase material was separated from the liquid by filtration through Whatman GF/C filters. The solids were then re-exposed to fresh liquid at the same liquid-to-solid ratio, and the procedure repeated for five cycles. The mixing involved slowly rotating a two liter sealed glass bottle containing one liter of water and 50 g of material on a shaker table. All tests were done in duplicate. The filtered leachates from each cycle of a sample were combined and stored in amber-colored bottles prior to analysis. Table VII lists the sequential batch extraction samples analyzed for dioxins and furans.

Table VII. List of sequential batch extraction samples.

| Material | Water type |
|---|---|
| Glen Cove fly ash | filtered seawater |
| Glen Cove fly ash | distilled |
| Baltimore combined ash | filtered seawater |
| Baltimore combined ash | distilled |
| Crushed sand-gravel proctor | filtered seawater |
| Crushed sand-gravel proctor | distilled |

## Ash Extraction and Sample Preparation

Solid samples were extracted in a soxhlet apparatus. Prior to sample introduction, 1 g of silica gel along with a glasswool plug was placed in a cellulose extraction thimble and extracted for one hour with 100 ml of toluene. The toluene was discarded. A 10 g sample of the ash was added to the thimble above the silica, topped with the glasswool plug, and spiked with 100 ng of each of the internal standards listed in Table VIII. The ash was subsequently extracted with 100 ml of toluene for 24 hours, and the crude extract concentrated to approximately 1 ml in a stream of dry nitrogen.

The concentrated extract was purified by column chromatography to eliminate compounds that might interfere in the detection of individual dioxins and furans. The procedure involves three columns; the first, a silica

**Table VIII.** Internal standards for GC/MS analysis.

1. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin ($^{13}C_{12}$, 99%)
2. 1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin ($^{13}C_{12}$, 99%)
3. 1,2,3,4,6,7,8,9-Octachlorodibenzo-*p*-dioxin ($^{13}C_{12}$, 99%)
4. 2,3,7,8-Tetrachlorodibenzofuran ($^{13}C_{12}$, 99%)
5. 2,3,4,7,8-Pentachlorodibenzofuran ($^{13}C_{12}$, 99%)
6. 1,2,3,4,6,7,8,9-Octachlorodibenzofuran ($^{13}C_{12}$, 99%)

gel column. A disposable glass tube (20 mm O.D. x 230 mm length) was packed as shown in Figure 3. The column was preeluted with 30 ml of hexane and rinsed with hexane before the sample extract (approximately 1 ml) was added with three 5 ml hexane rinses of the sample container. The initial eluate was discarded prior to elution with a further 90 ml of hexane. This entire fraction was retained and concentrated to 1 ml.

The second column consisted of a 3/8" O.D. disposable glass pipette packed with 3 g of precleaned, activated alumina and precleaned glasswool as shown in Figure 4. The column was preeluted with 10 ml of hexane prior to the addition of the concentrated eluate from the silica column together with three 1 ml hexane rinses. The column was then eluted with 15 ml

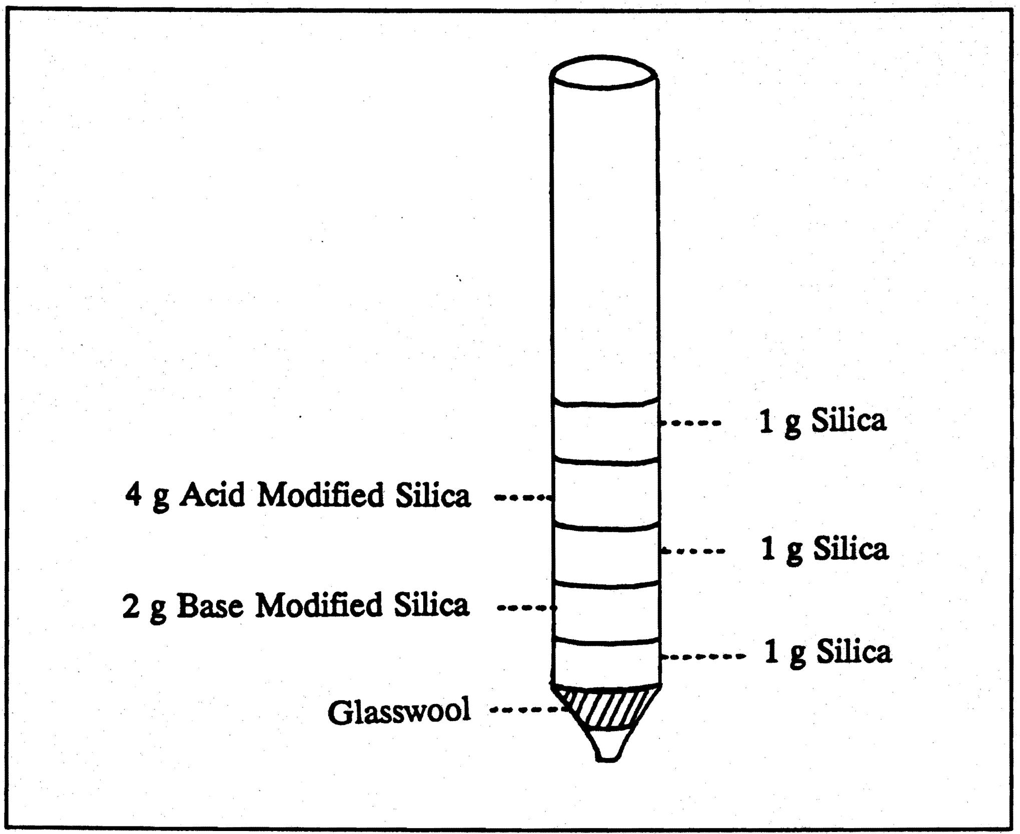


**Figure 3. Diagram of silica column.**

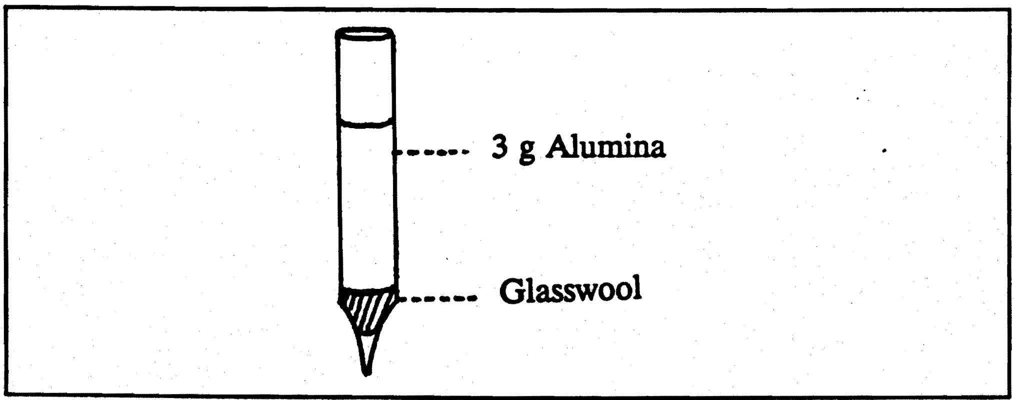


**Figure 4. Diagram of alumina column.**

hexane followed by 10 ml methylene chloride:hexane (2:25). The eluate to this point was discarded, and dioxins and furans were eluted with 15 ml methylene chloride:hexane (1:1). This fraction was concentrated to 0.5 ml. The last column, constructed in a 9" disposable glass pipette with the tapered end cut off, contained 2 cm length of carbon/celite mixture sandwiched between 2 glasswool plugs as shown in Figure 5. This column was preeluted with 2 ml benzene:ethyl acetate (1:1), 1 ml methylene chloride:cyclohexane (1:1), and 2 ml hexane successively before the concentrated eluate from the previous column (0.5 ml) was added together with three 1 ml hexane rinses. The column was eluted with 2 ml benzene:ethyl acetate (1:1) followed by 2 ml methylene chloride:cyclohexane (1:1). The eluate to this stage was discarded, and the column was inverted and eluted with 4 ml toluene. This fraction was concentrated to 1 ml and saved for GC-MS analysis.

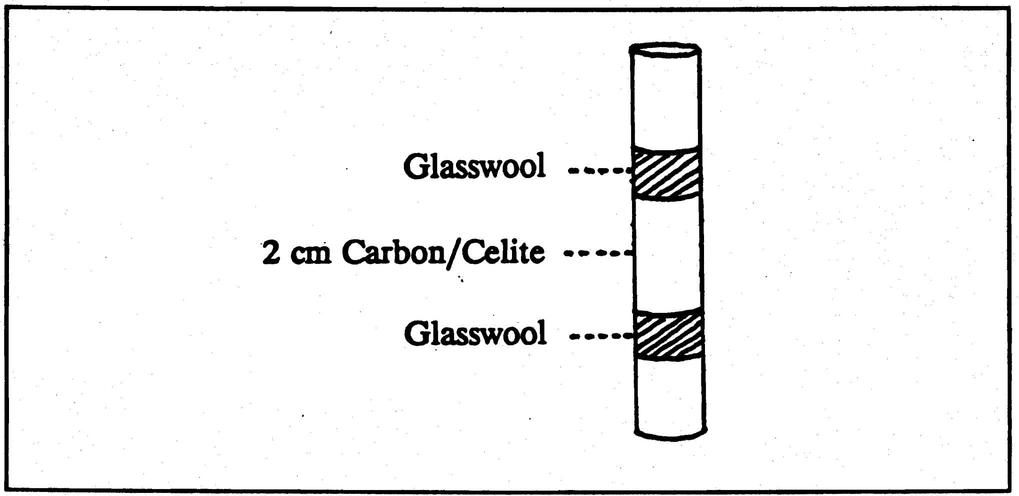


**Figure 5. Diagram of carbon/celite column.**

## Liquid Sample Preparation

Dioxins and furans were isolated from the sequential batch extraction leachates and tank leachates using a specially designed cartridge containing $C_{18}$ reverse phase adsorbent. This cartridge was used by the New York State Department of Health for trapping dioxins and furans in drinking water samples in the low parts-per-quadrillion (ppq) range (O'Keefe *et al.*, 1986). The cartridge, constructed of stainless steel, consists of a 9 cm Whatman GF/D 2.7 μm glass fiber filter supported on a metal screen, followed by a 2.5 cm Gelman Type A/E 1 μm glass fiber filter supported by a 2 μm stainless steel frit. A chamber beneath the filters was packed with 7.2 g of 40 μm Bondesil $C_{18}$ reverse-phase adsorbent, topped with a glasswool plug.

The cartridge was wet with 100 ml methanol followed by 300 ml distilled water before use. The first 20 ml of methanol was allowed to percolate through under gravity flow. The remainder of the methanol and the distilled water was pulled through the cartridge by vacuum.

The water sample was transferred to a stainless steel cylinder along with three methanol rinses of the sample container. A methanol solution containing 25 ng of each labelled internal standard was added dropwise to the water in the cylinder and mixed. The cylinder was then connected to the cartridge by stainless steel tubing, and the sample was forced through the cartridge by positive pressure from filtered, purified helium at 80 psi. The water was collected in a bottle and discarded after passing through the cartridge.

Organic compounds were eluted from the cartridge with 500 ml acetone. The acetone was added slowly to the cylinder, rinsing the sides in the process. A clean, amber-colored bottle was put into place to collect the eluate. The acetone was forced through the cartridge with a positive pressure of 20 psi of helium. After elution the cartridge was opened and the filters were removed, air-dried, and soxhlet extracted with 100 ml hexane for 18 hours. This extract, containing the dioxins and furans that were associated with the particles caught on the filters, was saved to be combined with the cartridge eluate.

The eluted acetone was replace by hexane on a boiling water bath, and the volume adjusted to approximately 60 ml. If water were present, it was removed using a separatory funnel, and the hexane was dried over sodium sulfate. This hexane solution was combined with the hexane from the filter extraction described above and purified by the following two-column procedure.

Extracts from the leachate studies were purified using two columns, the first being identical to the silica column described previously. The second column was constructed from a 9" disposable glass pipette and was packed with approximately 1 g precleaned, activated florisil and precleaned glasswool. The florisil was covered with a little sodium sulfate to absorb moisture as shown in Figure 6.

The column was preeluted with hexane and the concentrated eluate from the silica column (1 ml) was added to the florisil column along with two 1 ml hexane rinses. Forty ml of methylene chloride:hexane (1:50) was added, and the eluate, discarded. The column was eluted with 50 ml methylene chloride, which was saved and concentrated to a final volume of 100 μl for GC-MS analysis.

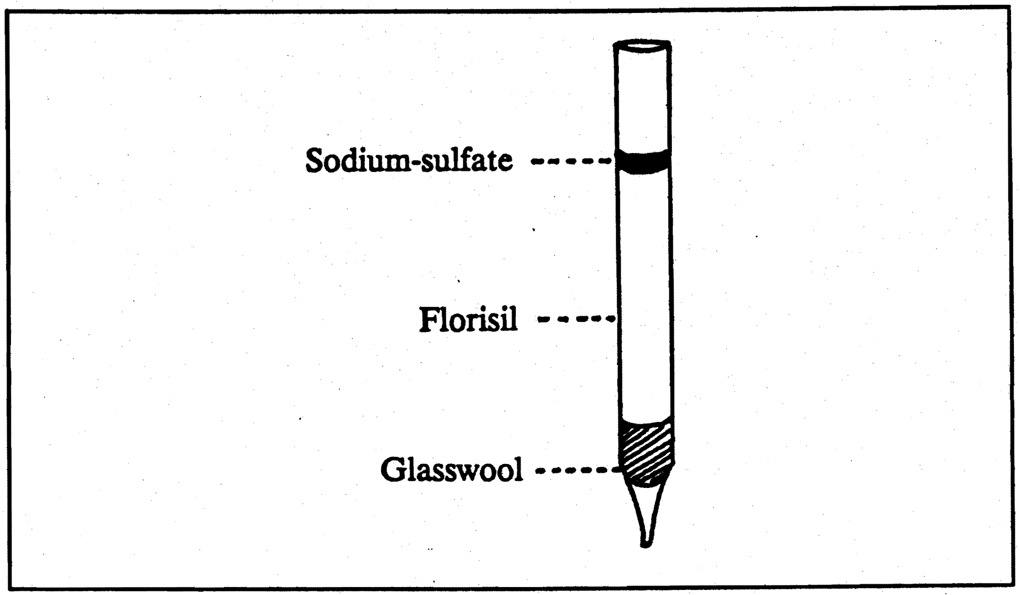


**Figure 6. Diagram of florisil column.**

## Gas Chromatography - Mass Spectrometer Analysis

Sample extracts that were purified by the column chromatography procedures were analyzed by gas chromatography/mass spectrometry (GC/MS). The mass spectrometer instrument used was a KRATOS MS 890 with a DS-90 data system. It was fitted with a Mega Series Carlo Erba gas chromatograph. A 60 m x 0.238 mm I.D. DB5 capillary column was used which has a film thickness of 0.25 μm (J & W Scientific, Folsom CA, 95630).

A one microliter splitless injection of the extract was used. $^{37}$Cl labelled TCDD was used as the external standard, and was co-injected with the sample. The injector temperature was 270°C and the temperature of the transfer line was 290°C. Helium was used as the carrier gas at a pressure of

200 pKa. The GC oven temperature was controlled by a program which rises from 190° to 220°C at 20° per minute. It then continues to rise to 310°C at 5° per minute.

The mass spectrometer was used in the selected ion monitoring mode (SIM). The GS/MS run was divided into five SIM groups. Table IX lists by monitoring group the mass of each ion used for quantitation and confirmation and its retention time. Retention time windows for each group have been determined using a standard that contains a mixture of each first and last eluting isomer from each group. Perflouro kerosene was used to calibrate the MS mass scale.

**Table IX. Masses, retention times, and theoretical isotope ratios for all ions being monitored for PCDD and PCDF analyses.**

| Compound | Mass 1 | Mass 2 | Isotope Ratio | Retention Time |
|---|---|---|---|---|
| TCDF | 303.9014 | 305.8984 | 0.77 | 22:40 |
| TCDD | 319.8965 | 321.8936 | 0.77 | 23:32 |
| $^{13}$C TCDF | 315.9417 | 317.9387 | 0.77 | 22:40 |
| $^{13}$C TCDD | 331.9368 | 333.9338 | 0.77 | 23:32 |
| $^{37}$Cl TCDD | 327.8845 | | | 23:34 |
| | | | | |
| PeCDF | 339.8596 | 341.8567 | 1.54 | 29:21 |
| PeCDD | 355.8545 | 357.8516 | 1.54 | 29:59 |
| $^{13}$C PeCDF | 345.8787 | 347.8767 | 1.54 | 29:21 |
| $^{13}$C PeCDD | 367.8948 | 369.8918 | 1.54 | 29:59 |
| | | | | |
| HxCDF | 373.8206 | 375.8176 | 1.23 | 34:57 |
| HxCDD | 389.8157 | 391.8125 | 1.23 | 36:28 |
| | | | | |
| HpCDF | 407.7817 | 409.7786 | 1.03 | 41:04 |
| HpCDD | 423.7766 | 425.7737 | 1.03 | 43:16 |
| | | | | |
| OCDF | 441.7428 | 443.7346 | 0.88 | 49:55 |
| OCDD | 457.7375 | 459.7346 | 0.88 | 49:41 |
| $^{13}$C OCDF | 453.7830 | 455.7800 | 0.88 | 49:53 |
| $^{13}$C OCDD | 469.7778 | 471.7749 | 0.88 | 49:41 |

# QUALITY CONTROL

The mass scale of each monitor group was calibrated daily on the GC/MS using perflourokerosene at a resolution of 1000. A native standard was coinjected periodically with the external standard for calibration checks to evaluate accuracy of quantification and isomer resolution. Solvent blanks are also injected periodically to measure background on the instrument. The external standard, $^{37}$Cl labelled TCDD, was co-injected with all samples as a method of monitoring injection technique and to use in calculating internal standard recoveries.

Percent recovery can be calculated on the basis of responses observed using the following formula, and assuming 100% recovery:

$$\frac{(S_{is}/S_{es})\ (100)}{(I/E)} = \%\ \text{recovery}$$

Where:

$S_{is}$ = Peak area for internal standard recovered from sample

$S_{es}$ = Peak area for external standard co-injected with sample

I = Peak area for internal standard from calibration run

E = Peak area for external standard from calibration run

Several native spike and method blank samples were processed during the extraction and cleanup of the samples. The native spike samples were used to evaluate the accuracy of quantification. The method blanks were used to demonstrate that the techniques used were free from contamination. All samples were done in duplicate.

In identifying PCDD and PCDF isomers, four criteria must be met by the pair of selected-ion chromatograms:

1. There must be a response in both the quantitation and confirmation ion chromatograms occurring within two seconds of each other.
2. The ratio of the intensity of the specific ion signals must be within 20% of the theoretically expected ratio.
3. The chromatographic retention times must be correct relative to the appropriate stable isotopically labelled internal standard and fall within the appropriate retention time windows.
4. The intensities of the ion signals must exceed the baseline noise by a factor of 2:1.

# RESULTS

## Municipal Solid Waste Incinerator Ash

Dioxin and furan concentrations were determined in various ash samples including fly ash, bottom ash, and combined ash from different municipal solid waste incinerators during normal operating conditions. Each ash sample was partially purified by the method described and analyzed by gas chromatography/ mass spectrometry (GC/MS). Results are presented in Tables XI-XX. For each incinerator site total concentrations of dioxin and furan congener groups are presented for each ash sample as an average of duplicate analyses. Average percent recoveries of the internal standards are also presented in Tables X-XIX. Average concentrations of selected 2,3,7,8-substituted isomers which coeluted with the internal standards are also presented for each ash samples. Those 2,3,7,8-substituted isomers that did not have a coeluting standard in these analyses, were not identifiable in this study. An ND entry signifies none detected and therefore the concentration of that isomer should be considered below detection limits. It should be noted that the DB-5 capillary gas chromatography column can not easily resolve the 2,3,7,8-substituted isomer from other tetrachlorinated dibenzofurans.

Therefore, concentrations reported for 2,3,7,8-TCDF may contain contributions from other isomers (Sawell, 1989).

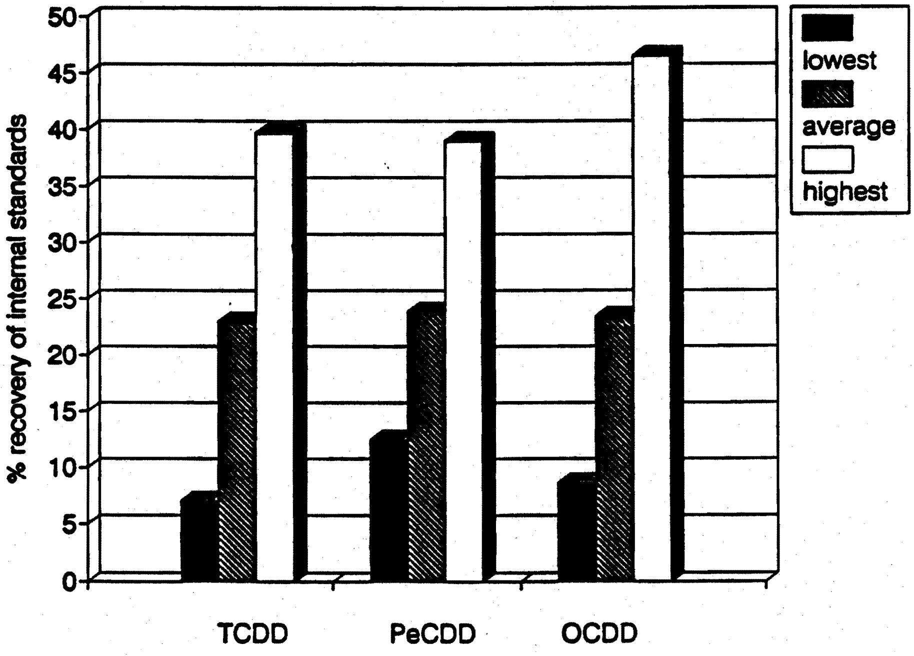
As a result of extraction, sample cleanup, presence of interfering compounds, and instrument background levels, detection limits varied among samples by as much as a factor of three. Table X lists the typical detection limit for the various dioxin and furan isomers.

**Table X. Typical detection limits for dioxin and furan isomers (ng/g).**

| Isomer | Detection Limit (ng/g) |
|---|---|
| TCDD | 0.5 |
| PeCDD | 0.5 |
| HxCDD | 0.5 |
| HpCDD | 1.0 |
| OCDD | 1.0 |
| TCDF | 0.2 |
| PeCDF | 0.2 |
| HxCDF | 0.5 |
| HpCDF | 0.5 |
| OCDF | 5.0 |

Recoveries of internal standards from raw ash samples varied among samples. Figure 7 presents the lowest, highest and average percent internal standard recovery values for each congener group. The wide range of values is due to the multiple chromatographic cleanups and inexperience with the tedious analytical techniques. As more experience was gained, and improvements were made in sample handling procedures, recoveries of internal standards improved.

**Figure 7. Percent recovery of internal standards in incinerator ash samples.**



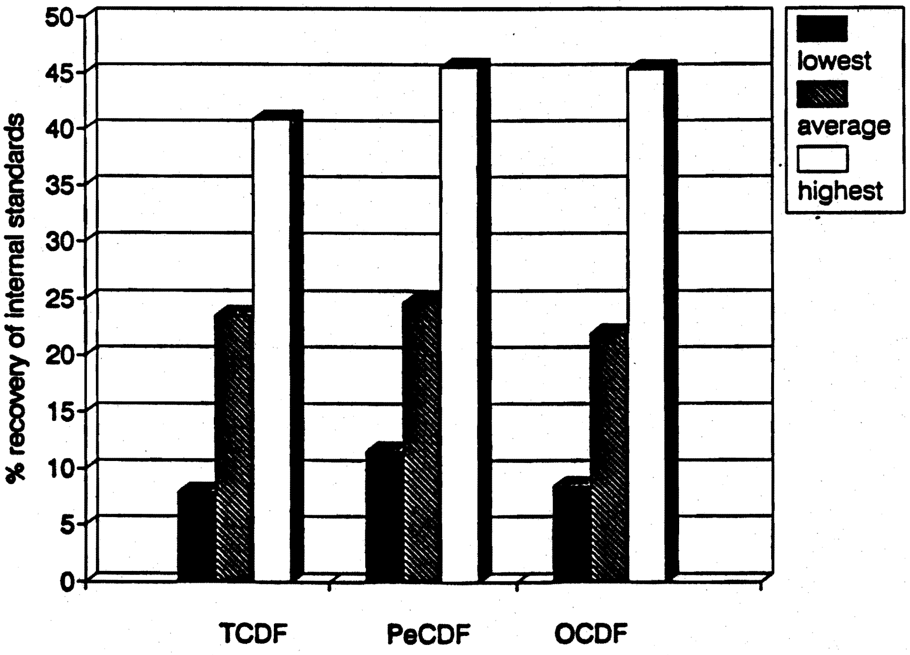


**Table XI. Dioxin and furan concentrations in two fly ash samples obtained from the Glen Cove incineration facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Glen Cove<br>GC-F-1 | total TCDD | 36.15 | 13.7 |
| | 2,3,7,8-TCDD | 7.00* | |
| | total PeCDD | 82.95 | 16.0 |
| | 1,2,3,7,8-PeCDD | 6.50 | |
| | total HxCDD | 158.85 | |
| | 1,2,3,6,7,8-HxCDD | 13.30 | |
| | total HpCDD | 149.85 | |
| | 1,2,3,4,6,7,8-HpCDD | 80.90 | |
| | total OCDD | 134.95 | 18.6 |
| | total TCDF | 44.7 | 15.1 |
| | 2,3,7,8-TCDF | 17.00 | |
| | total PeCDF | 62.40 | 17.0 |
| | 2,3,4,7,8-PeCDF | 9.00* | |
| | total HxCDF | 74.15 | |
| | 1,2,3,6,7,8-HxCDF | 8.90 | |
| | total HpCDF | 46.85 | |
| | 1,2,3,4,6,7,8-HpCDF | 33.40 | |
| | total OCDF | 26.70 | 17.6 |
| Glen Cove<br>GC-F-2 | total TCDD | 72.95 | 13.7 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 207.55 | 16.0 |
| | 1,2,3,7,8-PeCDD | 5.80 | |
| | total HxCDD | 308.30 | |
| | 1,2,3,6,7,8-HxCDD | 17.40 | |
| | total HpCDD | 545.55 | |
| | 1,2,3,4,6,7,8-HpCDD | 278.45 | |
| | total OCDD | 816.85 | 18.6 |
| | total TCDF | 63.2 | 15.1 |
| | 2,3,7,8-TCDF | 25.45 | |
| | total PeCDF | 156.45 | 17.0 |
| | 2,3,4,7,8-PeCDF | 15.10 | |
| | total HxCDF | 100.00 | |
| | 1,2,3,6,7,8-HxCDF | 20.00 | |
| | total HpCDF | 166.40 | |
| | 1,2,3,4,6,7,8-HpCDF | 113.90 | |
| | total OCDF | 170.95 | 17.6 |

ND = none detected * = detected in only one sample

**Table XII. Dioxin and furan concentrations in two combined ash samples obtained from the Glen Cove incineration facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Glen Cove<br>GC-C-1 | total TCDD | ND | 24.9 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 25.2 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 5.75 | |
| | 1,2,3,6,7,8-HxCDD | 1.00* | |
| | total HpCDD | 6.00 | |
| | 1,2,3,4,6,7,8-HpCDD | 3.20 | |
| | total OCDD | 11.40 | 16.0 |
| | total TCDF | ND | 28.5 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 27.6 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | 2.05 | |
| | 1,2,3,6,7,8-HxCDF | 1.20* | |
| | total HpCDF | 1.65 | |
| | 1,2,3,4,6,7,8-HpCDF | 1.65 | |
| | total OCDD | 4.10 | 14.8 |
| Glen Cove<br>GC-C-2 | total TCDD | 0.70* | 24.9 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 0.40* | 25.2 |
| | 1,2,3,7,8-PeCDD | 0.40* | |
| | total HxCDD | 9.05 | |
| | 1,2,3,6,7,8-HxCDD | 3.60 | |
| | total HpCDD | 28.65 | |
| | 1,2,3,4,6,7,8-HxCDD | 19.25 | |
| | total OCDD | 57.95 | 16.0 |
| | total TCDF | 0.40* | 28.5 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 27.6 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | 5.00 | |
| | 1,2,3,6,7,8-HxCDF | 3.10 | |
| | total HpCDF | 15.05 | |
| | 1,2,3,4,6,7,8-HpCDF | 7.10 | |
| | total OCDF | 15.50 | 14.8 |

ND = none detected * = detected in only one sample

**Table XIII. Dioxin and furan concentrations in two fly ash samples obtained from the first sampling of the Dutchess County facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Dutchess County 1DC-F-1 | total TCDD | 47.00* | 21.2 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 40.90 | 21.8 |
| | 1,2,3,7,8-PeCDD | 1.50* | |
| | total HxCDD | 48.15 | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | 1,2,3,7,8,9-HxCDD | ND | |
| | total HpCDD | 46.95 | |
| | 1,2,3,4,6,7,8-HpCDD | 23.30 | |
| | total OCDD | 18.50 | 19.4 |
| | total TCDF | 51.60 | 22.1 |
| | 2,3,7,8-TCDF | 10.85 | |
| | total PeCDF | 42.85 | 21.6 |
| | 2,3,4,7,8-PeCDF | 3.85 | |
| | total HxCDF | 30.10 | |
| | 1,2,3,6,7,8-HxCDF | 4.35 | |
| | total HpCDF | 13.30 | |
| | 1,2,3,4,6,7,8-HpCDF | 7.90 | |
| | total OCDF | 4.10 | 20.3 |
| Dutchess County 1DC-F-2 | total TCDD | 28.20 | 35.0 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 44.45 | 37.1 |
| | 1,2,3,7,8-PeCDD | 1.80 | |
| | total HxCDD | 69.50 | |
| | 1,2,3,6,7,8-HxCDD | 3.80 | |
| | 1,2,3,7,8,9-HxCDD | 5.45 | |
| | total HpCDD | 49.1 | |
| | 1,2,3,4,6,7,8-HpCDD | 23.9 | |
| | total OCDD | 21.6 | 46.5 |
| | total TCDF | 61.40 | 35.4 |
| | 2,3,7,8-TCDF | 12.80 | |
| | total PeCDF | 45.95 | 42.7 |
| | 2,3,4,7,8-PeCDF | 4.60 | |
| | total HxCDF | 34.65 | |
| | 1,2,3,6,7,8-HxCDF | 4.60 | |
| | total HpCDF | 14.2 | |
| | 1,2,3,4,6,7,8-HpCDF | 8.10 | |
| | total OCDF | 5.40 | 45.6 |

ND = none detected * = detected in only one sample

**Table XIV. Dioxin and furan concentrations in fly and bottom ash obtained from the second sampling of the Dutchess County facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Dutchess County 2DC-F-1 | total TCDD | 6.85 | 25.4 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 9.30 | 25.2 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 10.60 | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | 1,2,3,7,8,9-HxCDD | ND | |
| | total HpCDD | 4.90 | |
| | 1,2,3,4,6,7,8-HpCDD | 2.5 | |
| | total OCDD | 1.85 | 29.4 |
| | total TCDF | 42.05 | 26.5 |
| | 2,3,7,8-TCDF | 9.05 | |
| | total PeCDF | 21.75 | 31.5 |
| | 2,3,4,7,8-PeCDF | 2.20 | |
| | total HxCDF | 7.10 | |
| | 1,2,3,6,7,8-HxCDF | 0.90 | |
| | total HpCDF | 3.50 | |
| | 1,2,3,6,7,8-HpCDF | 2.10 | |
| | total OCDF | 1.75 | 26.4 |
| Dutchess County 2DC-B-1 | total TCDD | ND | 7.1 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 13.4 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | 1,2,3,7,8,9-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 15.7 |
| | total TCDF | ND | 8.0 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 22.6 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 15.0 |

ND = none detected * = detected in only one sample

**Table XV. Dioxin and furan concentrations in two combined ash samples obtained from the first sampling of the Dutchess County facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Dutchess County 1DC-C-1 | total TCDD | 1.10 | 29.1 |
| | 2,3,7,8-TCDD | 0.10* | |
| | total PeCDD | 0.30* | 36.5 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 4.10* | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | 3.70 | |
| | 1,2,3,4,6,7,8-HpCDD | 2.20 | |
| | total OCDD | 4.50 | 26.6 |
| | total TCDF | 2.70 | 23.6 |
| | 2,3,7,8-TCDF | 1.00 | |
| | total PeCDF | ND | 27.7 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | 1.20* | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | 1.20* | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 24.3 |
| Dutchess County 1DC-C-2 | total TCDD | ND | 10.8 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 0.10* | 12.5 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 6.10 | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | 5.20 | |
| | 1,2,3,4,6,7,8-HpCDD | 3.00 | |
| | total OCDD | 5.80 | 8.7 |
| | total TCDF | 1.90 | 11.5 |
| | 2,3,7,8-TCDF | 0.90 | |
| | total PeCDF | 0.80 | 11.6 |
| | 2,3,4,7,8-PeCDF | 0.8 | |
| | total HxCDF | 0.60* | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 8.5 |

ND = none detected * = detected in only one sample

**Table XVI. Dioxin and furan concentrations in two fly ash samples from the New England I incineration facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| New England I NE I-F-1 | total TCDD | ND | 20.4 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 22.7 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 33.0 |
| | total TCDF | ND | 18.6 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 23.6 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 27.2 |
| New England I NE I-F-2 | total TCDD | ND | 15.4 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 13.6 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 2.50* | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 16.7 |
| | total TCDF | ND | 18.0 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 12.2 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | 0.5* | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 13.3 |

ND = none detected * = detected in only one sample

**Table XVII. Dioxin and furan concentrations in a combined ash and a bottom ash sample from the New England I incineration facility.**

| Facility<br>& sample | Homolog<br>& isomer | Conc.<br>(ng/g) | % recovery<br>int. std. |
|---|---|---|---|
| New England I NE I-C | total TCDD | ND | 26.2 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 24.3 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 26.5 |
| | total TCDF | ND | 23.2 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 16.4 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 20.4 |
| New England I NE I-B | total TCDD | ND | 20.0 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 14.9 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 12.9 |
| | total TCDF | ND | 19.5 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 13.7 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 20.4 |

ND = none detected * = detected in only one sample

**Table XVIII. Dioxin and furan concentrations in fly and bottom ash samples from the first sampling of the New England II facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| New England II NE II-F | total TCDD | ND | 18.8 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 20.0 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8 HxCDD | ND | |
| | total OCDD | ND | 21.4 |
| | total TCDF | ND | 17.9 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 17.3 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,4,6,7,8-HxCDF | ND | |
| | total HpCDF | 0.85 | |
| | 1,2,3,4,6,7,8-HpCDF | 1.00* | |
| | total OCDF | ND | 20.8 |
| New England II NE II-B | total TCDD | ND | 34.1 |
| | 2,4,7,8-TCDD | ND | |
| | total PeCDD | ND | 32.1 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 35.3 |
| | total TCDF | ND | 40.4 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 36.4 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 45.3 |

ND = none detected * = detected in only one sample

**Table XIX. Dioxin and furan concentrations in fly and bottom ash samples obtained from the second sampling of the New England II facility.**

| Facility & sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| New England II 2NE II-F | total TCDD | ND | 39.7 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 39.0 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 0.10* | |
| | 1,2,3,6,7,8 HxCDD | 0.10* | |
| | total OCDD | 0.40* | 35.5 |
| | total TCDF | 1.90* | 40.9 |
| | 2,3,7,8-TCDF | 0.60* | |
| | total PeCDF | 0.50* | 45.5 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | 0.80 | |
| | 1,2,3,4,6,7,8-HpCDF | 0.70* | |
| | total OCDF | ND | 35.4 |
| New England II 2NE II-B | total TCDD | ND | 26.8 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | ND | 29.9 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 23.5 |
| | total TCDF | ND | 31.4 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 33.2 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 21.6 |

ND = none detected * = detected in only one sample

**Table XX. Dioxin and furan concentrations in a combined ash sample from the Baltimore incineration facility.**

| Facility sample | Homolog & isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Baltimore<br>Balt-C | total TCDD | ND | 22.5 |
| | 2,4,7,8-TCDD | ND | |
| | total PeCDD | ND | 22.3 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | ND | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | ND | |
| | 1,2,3,4,6,7,8-HpCDD | ND | |
| | total OCDD | ND | 14.6 |
| | total TCDF | ND | 19.6 |
| | 2,3,7,8-TCDF | ND | |
| | total PeCDF | ND | 18.9 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | ND | |
| | 1,2,3,4,6,7,8-HpCDF | ND | |
| | total OCDF | ND | 12.7 |

ND = none detected * = detected in only one sample

## Fly Ash Fractionation Study

One fly ash sample collected from the New England I facility was subjected to analyses to determine the concentration of dioxins and furans as a function of particle size. The fly ash was passed through mesh screens, resulting in three samples with particle size ranges of <45 μm, 45-75 μm, and 75-150 μm (particles >150μm were discarded). Each size fraction was analyzed separately using the same technique as used for the other ash samples. Table XXI presents average concentration levels of dioxins and furans and percent recoveries of internal standards from these size fractionated samples. Figure 8 shows the highest, lowest and average values for percent recoveries of internal standards according to congener group. Recoveries of internal standards from the fractionated ash were significantly higher than those reported for the raw ash samples due to experience and improved sample handling procedures.

**Figure 8. Percent recovery of internal standards in fractionated fly ash samples.**

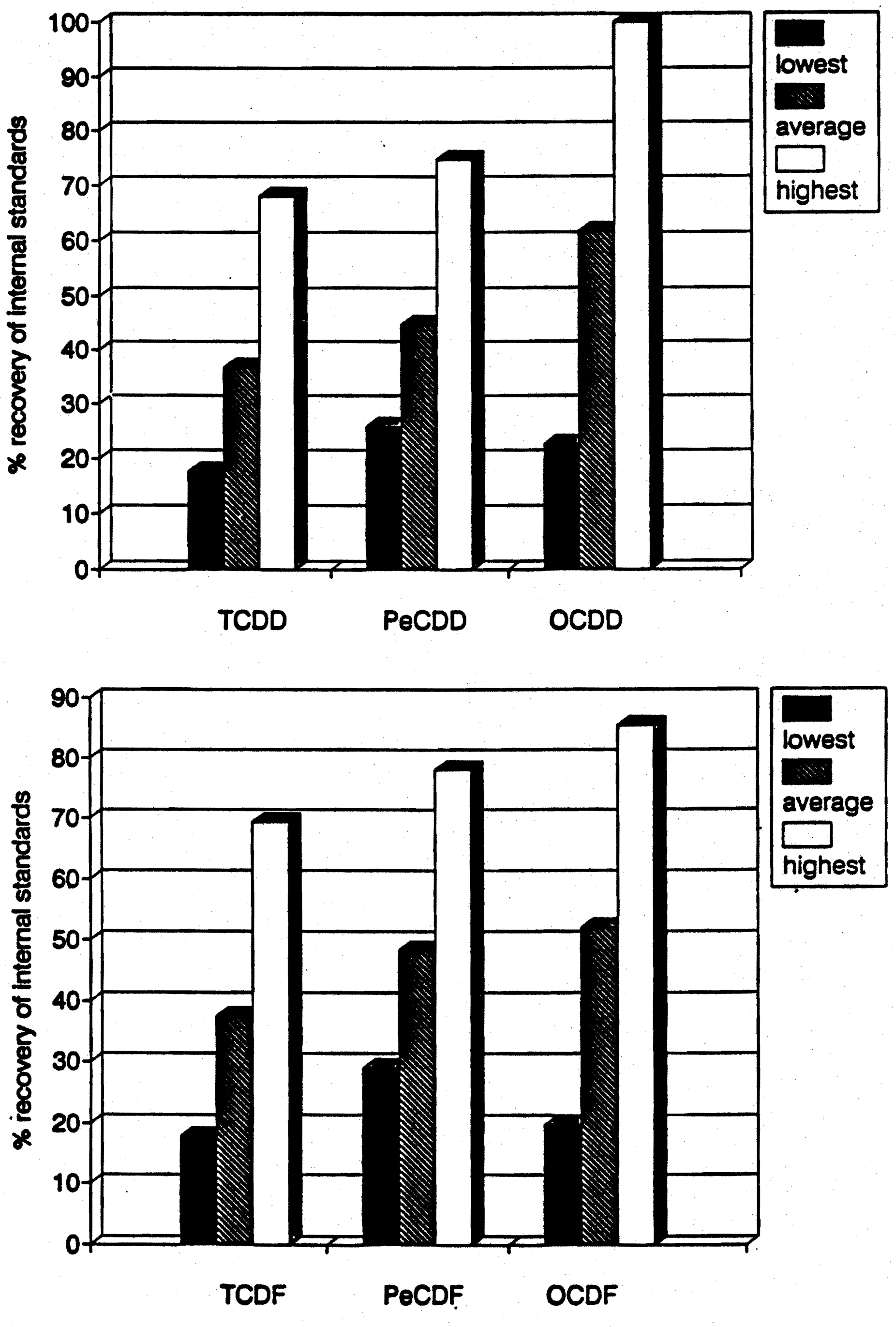


**Table XXI. Dioxin and furan concentrations in fractionated fly ash obtained from the New England I incinerator facility.**

| particle size (μm) | homolog and isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| <45 | total TCDD | 4.7 | 24.5 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 5.6 | 25.9 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 9.2 | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | 5.2 | |
| | 1,2,3,4,6,7,8-HpCDD | 2.1 | |
| | total OCDD | ND | 22.6 |
| | total TCDF | 1.6 | 25.3 |
| | 2,3,7,8-TCDF | 1.6 | |
| | total PeCDF | ND | 29.0 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | ND | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | 2.2 | |
| | 1,2,3,4,6,7,8-HpCDF | 2.2 | |
| | total OCDF | ND | 19.8 |
| 45-75 | total TCDD | 1.5 | 17.7 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 2.6 | 33.4 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 8.2 | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | 3.1 | |
| | 1,2,3,4,6,7,8-HpCDD | 1.9 | |
| | total OCDD | 2.3 | 62.3 |
| | total TCDF | 1.4 | 17.8 |
| | 2,3,7,8-TCDF | 0.9 | |
| | total PeCDF | 0.4 | 38.3 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | 1.4 | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | 2.4 | |
| | 1,2,3,4,6,7,8-HpCDF | 1.2 | |
| | total OCDF | 0.9 | 50.9 |

ND = none detected

**Table XXI continued**

| particle size (μm) | homolog and isomer | Conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| 75-150 | total TCDD | 0.9 | 68.0 |
| | 2,3,7,8-TCDD | ND | |
| | total PeCDD | 2.1 | 74.7 |
| | 1,2,3,7,8-PeCDD | ND | |
| | total HxCDD | 6.2 | |
| | 1,2,3,6,7,8-HxCDD | ND | |
| | total HpCDD | 2.7 | |
| | 1,2,3,4,6,7,8-HpCDD | 1.5 | |
| | total OCDD | 2.0 | 100.6 |
| | total TCDF | 2.3 | 69.5 |
| | 2,3,7,8-TCDF | 0.9 | |
| | total PeCDF | 0.6 | 78.0 |
| | 2,3,4,7,8-PeCDF | ND | |
| | total HxCDF | 1.2 | |
| | 1,2,3,6,7,8-HxCDF | ND | |
| | total HpCDF | 2.9 | |
| | 1,2,3,4,6,7,8-HpCDF | 1.6 | |
| | total OCDF | 1.5 | 85.5 |

ND = none detected

## Tank Leachate Study

Concentrations of dioxins and furans were below detection in the tank leachates. Table XXII and XXIII present the tank leachate and sequential batch extraction results respectively. Stabilized ash proctors and sand-gravel cement proctors were submerged in distilled water and filtered seawater. After ten months of submersion, a stabilized ash proctor and a sand-gravel proctor from both distilled water and seawater tanks were removed. The water from each of those four tanks was analyzed separately for dioxins and furans. Detection limits and recoveries of internal standards are comparable to those obtained in the raw ash samples. No dioxins or furans were detected in the cement, sand or gravel used in the formation of stabilized incinerator ash and control cement proctor blocks.

**Table XXII. Dioxin and furan concentrations in distilled water from tank leachate studies of stabilized incinerator ash (SIA) and cement proctors.**

| leachate identification | homolog | conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| SIA proctor | total TCDD | ND | 10.6 |
| | total PeCDD | ND | 3.0 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 7.4 |
| | total TCDF | ND | 10.9 |
| | total PeCDF | ND | 27.5 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 4.0 |
| Cement (sand-gravel) proctor | total TCDD | ND | 20.6 |
| | total PeCDD | ND | 12.3 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 13.7 |
| | total TCDF | ND | 18.2 |
| | total PeCDF | ND | 19.7 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 10.0 |

ND = none detected

**Table XXIII. Dioxin and furan concentrations in seawater from tank leachate studies of stabilized incinerator ash (SIA) and cement protors.**

| leachate identification | homolog | conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| SIA proctor | total TCDD | ND | 15.1 |
| | total PeCDD | ND | 15.3 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 12.4 |
| | total TCDF | ND | 17.0 |
| | total PeCDF | ND | 15.4 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 13.2 |
| Cement (sand-gravel) proctor | total TCDD | ND | 30.1 |
| | total PeCDD | ND | 18.1 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 12.3 |
| | total TCDF | ND | 17.6 |
| | total PeCDF | ND | 13.5 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 12.3 |

ND = none detected

## Sequential Batch Extraction Study

Concentrations of dioxins and furans were below detection in all sequential batch extractions. Tables XXIV and XXV present the results in distilled water and seawater, respectively. Each sample analyzed is comprised of five 18 hour cycles of 1:20 material-to-water extractions as described earlier. The materials tested included Glen Cove fly ash, Baltimore combined ash, and crushed stabilized sand-gravel. Internal standard recovery was comparable to that obtained in the raw ash samples. Internal standard recoveries could not be calculated for the Glen Cove fly ash extraction in distilled water due to unusually low peaks for the external standard in the chromatograms. This is most likely due to incomplete injection of the $^{37}$Cl-labeled external standard or blow out of the septum. The chromatograms for all other ions were similar to those obtained form the other sequential batch extraction samples. Therefore no detection can be reported with confidence.

**Table XXIV. Dioxin and furan concentration in distilled water from sequential batch extractions of Baltimore combined ash, Glen Cove fly ash and crushed cement proctor.**

| extract indentification | homolog | conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Baltimore combined ash | total TCDD | ND | 76.9 |
| | total PeCDD | ND | 105.1 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 70.6 |
| | total TCDF | ND | 75.2 |
| | total PeCDF | ND | 14.2 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 57.9 |
| Glen Cove fly ash | total TCDD | ND | ** |
| | total PeCDD | ND | ** |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | ** |
| | total TCDF | ND | ** |
| | total PeCDF | ND | ** |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | ** |
| crushed cement proctor | total TCDD | ND | 32.5 |
| | total PeCDD | ND | 34.8 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 90.7 |
| | total TCDF | ND | 34.0 |
| | total PeCDF | ND | 57.3 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 161.6 |

ND = none detected ** = unable to calculate

**Table XXV. Dioxin and furan concentration in seawater from sequential batch extractions of Baltimore combined ash, Glen Cove fly ash, and crushed cement proctor.**

| extract indentification | homolog | conc. (ng/g) | % recovery int. std. |
|---|---|---|---|
| Baltimore combined ash | total TCDD | ND | 43.8 |
| | total PeCDD | ND | 47.8 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 33.7 |
| | total TCDF | ND | 19.7 |
| | total PeCDF | ND | 48.3 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 25.4 |
| Glen Cove fly ash | total TCDD | ND | 69.5 |
| | total PeCDD | ND | 47.4 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 35.1 |
| | total TCDF | ND | 30.2 |
| | total PeCDF | ND | 51.0 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 39.2 |
| Crushed cement proctor | total TCDD | ND | 27.5 |
| | total PeCDD | ND | 32.5 |
| | total HxCDD | ND | |
| | total HpCDD | ND | |
| | total OCDD | ND | 13.7 |
| | total TCDF | ND | 24.3 |
| | total PeCDF | ND | 27.6 |
| | total HxCDF | ND | |
| | total HpCDF | ND | |
| | total OCDF | ND | 12.5 |

ND = none detected

# DISCUSSION

## Municipal Solid Waste Incinerator Ash

The concentration of selected dioxin and furan congeners have been measured in ash samples from five different municipal waste incinerators. Results of the analyses indicate that significant concentrations of furans and dioxins may be found in fly ash and combined ash; however, bottom ash contains little or none of these compounds. Specific concentration in fly ash and combined ash may vary greatly among incinerators; Figures 9 and 10 summarize the total dioxin and furan concentrations in fly ash and combined ash, respectively, for each facility. The wide range of dioxin and furan concentrations measured in this work is consistent with previous studies of dioxins and furans in incinerator ash (Denison, 1988; Nottrodt *et al.*, 1989; Ontario Ministry of the Environment, 1985). It is recognized that all incinerators produce some dioxins and furans; however, older incinerators may produce residues with higher concentrations (Ontario Ministry of the Environment, 1985). This is most likely due to operating conditions and the design of the plant.

Figure 9. Total dioxins and furans in fly ash samples.

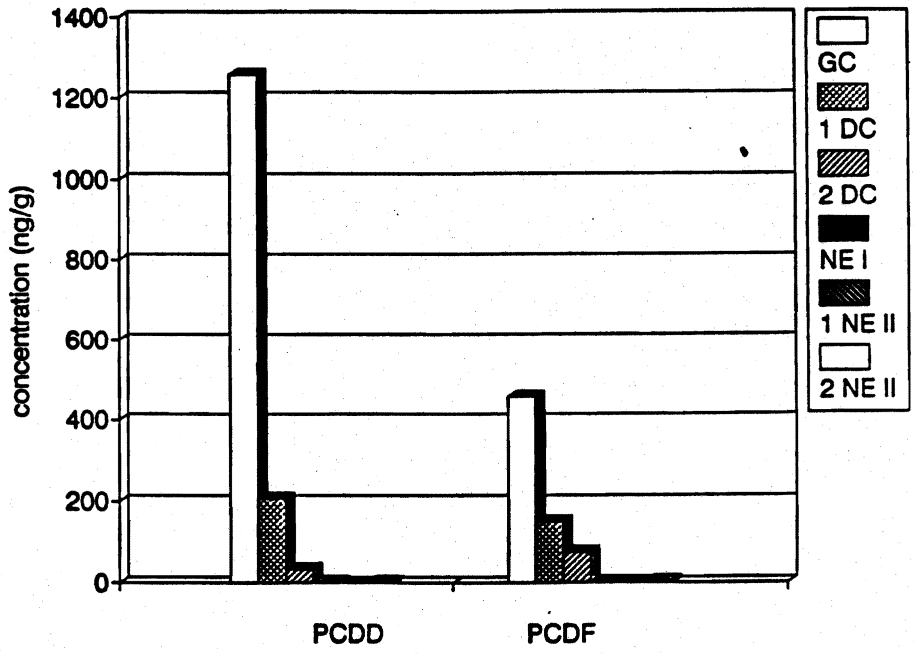
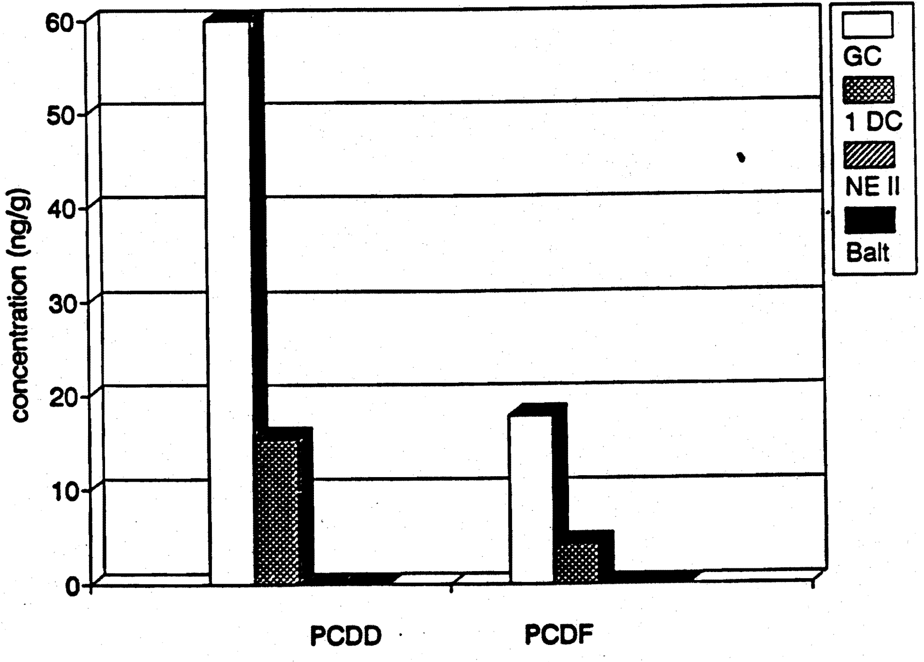


Figure 10. Total dioxins and furans in combined ash samples.



Residues from Glen Cove contained the highest concentrations of dioxins and furans, approximately 2-3 orders of magnitude higher than the New England samples, and about four times that of the Dutchess County samples. This is attributed the age of the facility; however, it is also the only facility sampled that burns sewage sludge along with the municipal solid waste. Although Glen Cove fly ash generally contains the highest concentrations of dioxins and furans in this study, this fly ash contains considerably less than the worldwide average concentrations of most isomers as compiled by the Ontario Ministry of the Environment (1985) comparing both old and new technologies. The octachlorinated dioxin and furan concentrations in Glen Cove fly ash are the exception, however, at approximately twice that of the worldwide average levels.

Results from Dutchess County fly ash reveal that not all relatively new facilities produce low concentrations of dioxins and furans. Although concentrations from the Dutchess County facility are considerably lower than Glen Cove levels, they are at least 50 times that of the New England I and II levels.

Residues from the New England facilities generally have very low levels of dioxin and furan contamination. One of two fly ash samples from New England I contained 2.5 ppb hexachlorinated dioxin and 0.5 ppb heptachlorinated furan; corresponding to < 0.1 ppb 2,3,7,8-TCDD toxic equivalents. No dioxins or furans were detected in combined or bottom ash from that facility. Similarly one fly ash sample from the New England II facility contained extremely low concentrations of a series of higher chlorinated dioxins and furans, however 2,3,7,8-TCDD toxic equivalents were calculated to be <0.1 ppb. No dioxins or furans were detected in New England II bottom ash.

The Baltimore facility, in which only combined ash was analyzed, contained concentrations below the detection limits of the this study. This is pointed out specifically because this ash was used in the formation of stabilized ash for the leachate studies. Identical Baltimore ash samples were analyzed by Roethel *et al.*(1990) and found to contain measurable amounts of 2,3,7,8-substituted dioxins and furans in the part per trillion range (pptr), below the detection limits of the current study. Table XXVI presents a summary of their findings.

Congener group concentrations varied among facilities. Glen Cove fly ash contained relatively greater fractions of the higher chlorinated dioxins than the other incinerators. Dutchess County fly ash contained greater fractions of the lower chlorinated furans. These variations, however, are within those observed in other ash studies (Ontario Ministry of the

**Table XXVI. Concentration of selected dioxins and furans in combined Baltimore ash as measured by Roethel *et al.* (1990).**

| Homolog group | Concentration (pg/g) |
|---|---|
| Total TCDD | 55.0 |
| Total PeCDD | 62.5 |
| Total HxCDD | 220.0 |
| Total HpCDD | 620.0 |
| Total OCDD | 1250.0 |
| Total TCDF | 271.6 |
| Total PeCDF | 260.0 |
| Total HxCDF | 245.0 |
| Total HpCDF | 280.0 |
| Total OCDD | 124.0 |

Environment, 1985). Although the mechanisms of formation are not well understood, temperature, carrier gas, and precursor structure seem to play a major role in determining the dioxin and furan isomers formed and their abundances (Ross *et al.*, 1989). Therefore isomeric patterns will vary among incinerators due to the composition of the municipal waste burned, the presence of oxygen and precursor compounds, and the operating conditions of the plant.

Since toxicities vary among congener groups and isomers, 2,3,7,8-TCDD toxic equivalents were determined using the US EPA method (Bellin and Barnes, 1987). Total equivalents for each facility is presented in Table XXVII. 2,3,7,8-Substituted isomers were not able to be identified in all samples. For the purpose of calculating toxic equivalents in these samples, it was estimated that those 2,3,7,8-substituted isomers that could not be identified or quantified were present at a concentration equal to their statistically expected fraction of the observed total concentration of the homolog group, assuming equal abundances of all isomers.

## Fractionated Fly Ash Study

In the past few years much research has been done on the formation of dioxins and furans in municipal solid waste incinerators. This research has shown that catalyzed surface reactions are probably the most important mechanisms in their formation (Dickson *et al.*, 1989). It is believed that precursors are formed within the combustion chamber and then react the form dioxins and furans in the post-combustion area (Ballschmiter *et al.*, 1988; Karasek and Dickson, 1987). The fly ash acts as a catalyst and is generally therefore the incinerator residue that contains the dioxins and furans. This is exhibited in the present study. No dioxins or furans were detected in any

**Table XXVII. Average 2,3,7,8-TCDD toxic equivalencies in fly and combined ash samples (ng/g).**

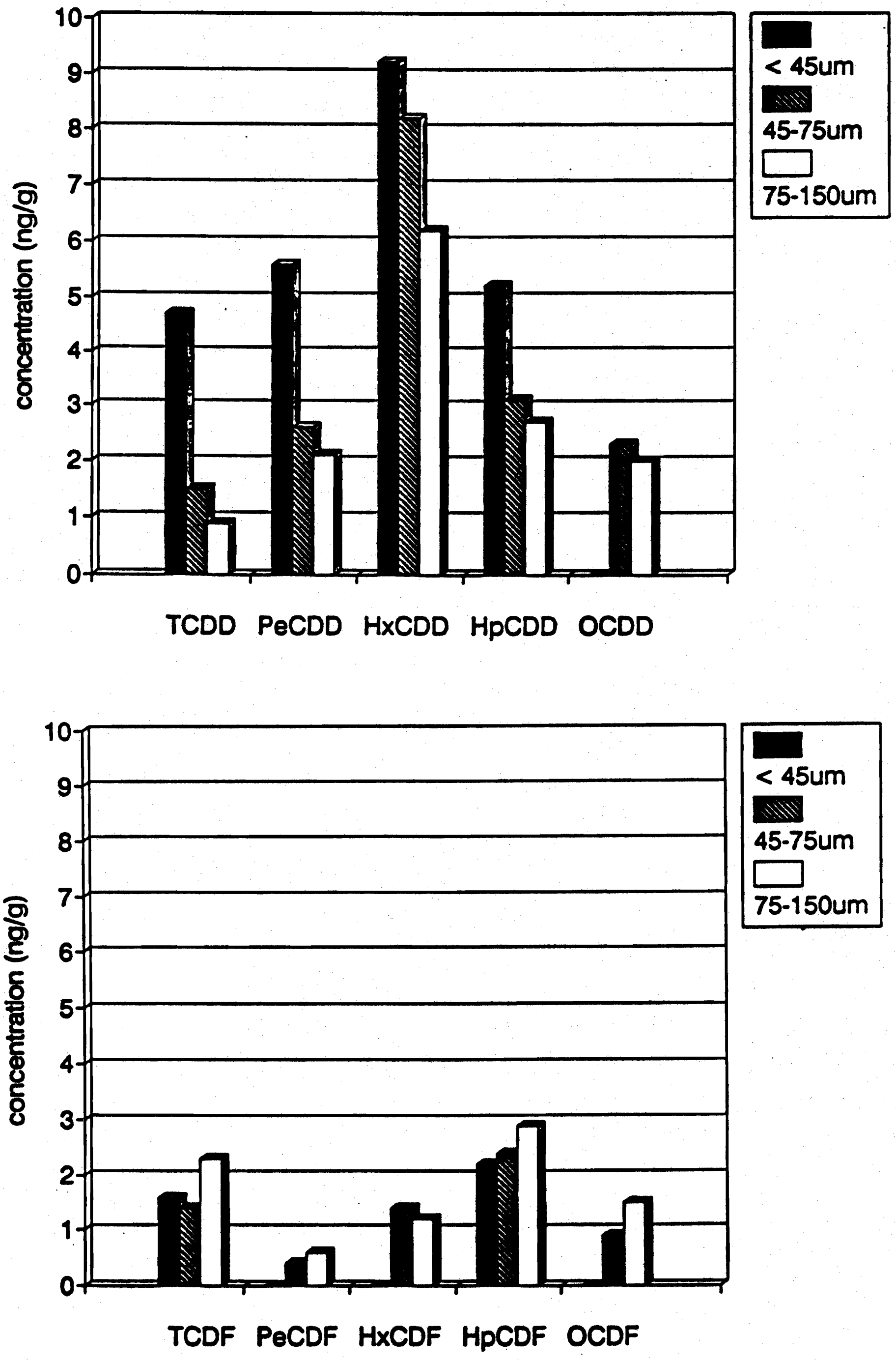
| Facility | Ash type | 2,3,7,8-TCDD equivalents |
|---|---|---|
| Glen Cove | F | 14.2 |
| | C | 0.5 |
| 1 Dutchess County | F | 2.8 |
| | C | 0.3 |
| 2 Dutchess County | F | 2.5 |
| New England I | F | ND |
| | C | ND |
| 1 New England II | F | <0.1 |
| 2 New England II | F | <0.1 |
| Baltimore | C | ND |

F = fly ash; C = combined ash; ND = none detected

bottom ash sample. The fly ash contained the greatest dioxin and furan concentrations of all the residue types; and the compounds detected in combined ash can be attributed to the fly ash component.

The New England I fractionated fly ash reveals that fly ash particles of <150 μm account for much of the dioxin and furan concentrations within the ash. Figure 11 summarizes the total dioxin and furan concentrations in the

**Figure 11. Total dioxin and furan concentrations in fractionated fly ash samples.**



fractionated fly ash. The 2,3,7,8-TCDD toxic equivalents for the <45 μm, 45-75 μm, and 75-150 μm particle sizes are 0.3, 0.4, and 0.8 respectively. The results indicate that dioxins and furans are significantly enriched within the fly ash particles of <150μm. This is of major importance since it is this finer ash fraction that is likely to become airborne, contributing to dry deposition of dioxins and furans to aquatic systems. It is also this fraction that is likely to become mobilized by water runoff during disposal or usage. Fly ash may actually be the major source of dioxins and furans in combined ash. All dioxins and furans detected in the combined ash from Glen Cove and Dutchess County can be accounted for by assuming an 8-12% fly ash component (no compounds were detected in New England I and II or Baltimore combined ashes).

## Tank Leachate and Sequential Batch Extraction Study

Although significant amounts of dioxins and furans were found in several municipal solid waste (MSW) incinerator residues in this study, none of these compounds were detected in distilled water or seawater sequential batch extractions of ash or stabilized incineration ash tank leachates.

These results can not simply be explained by the low solubility of the compounds of concern. Baltimore combined ash analyzed by Roethel *et al.* (1990) was found to contain an average of 11.2 pg of 2,3,7,8-TCDD per gram of ash (11.2 pptr). In a sequential batch extraction procedure, 50 grams of ash is used, therefore a total of 560 pg of 2,3,7,8-TCDD would be present. If one considers the solubility of 2,3,7,8-TCDD (0.2 $\mu$g/l) and assumes that this compound is readily released from ash, all 2,3,7,8-TCDD would be released into the water by the end of the five cycles of the extraction procedure. If a 30% recovery after separation and cleanup is expected, then there would be 0.17 ng 2,3,7,8-TCDD present within the sample. This concentration is below the detection limits of this study and may be unmeasurable.

However, if Glen Cove fly ash were extracted under the same assumptions, detectable levels of 2,3,7,8-TCDD would be present within the final sample. The Glen Cove fly ash utilized in this investigation contained 7.0 ng 3,2,7,8-TCDD per gram ash, totalling 350 ng in 50 g of ash. Assuming 30% recovery after separation and cleanup, 105 ng 2,3,7,8-TCDD would be present in the final sample. This concentration is well above the detection limits of this study. The question then becomes why were there no dioxins or furans detected within the sequential batch extracts of the Glen Cove fly ash?

Internal standards were added to all water samples prior to separation and cleanup. Percent recoveries of those standards were not high, but were comparable to those obtained from the ash/toluene extractions. Therefore, the separation and analytical technique utilized can efficiently remove and detect dioxins and furans from aqueous samples. The analytical technique can not be considered the reason for not detecting the compounds in the aqueous samples. Since dioxins and furans are detectable within aqueous samples, as shown by the internal standard recovery data, the question then becomes whether the compounds are actually readily released from the ash matrix?

Similar leaching studies have been conducted by other investigators. Sawell and Constable (1988) were also unable to detect dioxins and furans in distilled water leachates using the same sequential batch extraction techniques, with detection limits ranging from 0.5 to 2 ng/l. The MSW incinerator ashes utilized in that study had concentrations from below detection to 1040 ng of dioxin per gram of ash; and below detection to 280 ng furan per gram of ash. These levels are comparable to those in the Glen Cove fly ash used in the present study.

In comparison, Carsh *et al.* (1986) obtained low concentrations of the higher chlorinated dioxins and furans in the leachates of MSW incinerator fly ash with distilled water at 1:10 ash-to-solvent ratio. The MSW fly ash had concentrations from 5-410 ng dioxin per gram ash; and 7-270 ng furan per gram ash. Detection limits were not reported, however the quantitation limit for the leachate samples was 2 ng per sample. Trace levels of dioxins and furans were also detected in boiler ash leachates by Sawell *et al.* (1989). These studies indicate that dioxins and furans are released from incinerator ash and boiler ash under certain conditions. It is suggested that the release may be dependent upon the composition of the ash.

Since most incinerator residues are presently disposed of in landfills, investigators (AWD Technology, 1990; NUS Corporation, 1990) have analyzed leachates from a monofill that is exclusively used for the disposal of fly and combined incinerator ash. Leachates generated from rain falling on the surface of the ashfill is removed using a leachate collection system, and pumped into a wastewater holding pond. Leachates have been monitored for three years. Dioxins and furans were only detected in the first year sampling; hepta- and octachlorinated dioxins and heptachlorinated furan were detected at 0.2, 0.1 and 0.08 ppb, respectively, in samples collected from the leachate collection system. However no dioxins and furans were found in subsequent year samplings with detection limits ranging from 0.01 to 0.2 pptr.

Investigations by Kuehl *et al.* (1985) suggest that dioxins and furans are not readily released from incinerator ashes and are tightly bound to carbon.

Dioxins and furans are very difficult to remove from the residues with high concentrations of carbon.

Several studies have shown that dioxins bound to ash and organic detritus are also not readily available to organisms. Kuehl *et al.*(1985) exposed carp to one gram of fly ash for 30 days. The fish had a residue level of 2 pg/g. Another group of carp were exposed to an organic solvent extract of the same amount of identical ash, under the same conditions. These fish had a 10-fold increase in residue levels, 200 pg/g. A difference between the fly ash bound and free TCDD was proposed to explain the difference.

Similar experiments were conducted by Helder (1982) with rainbow trout yolk sac fry. The presence of a relatively large amount of fly ash did not impair growth, health or behavior in the fry and development was analogous to that of the control groups. However, minute amounts of organic solvent extracts of the same ash were administered, all fry died when exposed for at least four days.

The present investigation suggests that the dioxins associated with incinerator ash do not readily leach out into the surrounding water. Other studies have shown that these compounds are also not readily bioavailable when associated in this way. Roethel *et al.*, 1990 has suggested that the stabilization of the ash even further reduces leachability.

## Field Studies

To investigate the mobility of dioxins and furans from stabilized incineration ash in the marine environment, a set of artificial reefs were established in eight meters of water in Conscience Bay, Long Island Sound. Baltimore combined ash was used to produce stabilized incineration ash (SIA) blocks and placed underwater. Commercial cement blocks were used to construct a control reef approximately two meters from the SIA reef. SIA and cement blocks are removed from the water on a regular basis for physical and chemical testing. Included among these tests, the blocks are crushed and analyzed for dioxin and furan loss. Analyses done by Roethel *et al.* (1990) did not detect a significant loss of dioxins and furans after 192 days of submersion. The blocks have shown to hold their structural integrity, with compressive strength increasing by 5% over a 13 month period.

The reef is exposed to considerable tidal flushing with currents exceeding 3 meters per second (Roethel, 1981). The sediments in that area are poorly-sorted gravel and course sand. It has been shown in previous studies that weathering and sediment contact do not cause disintegration of the blocks which would expose additional block surface to leaching (Roethel *et al.*, 1990). The fact that no furans or dioxins were detected in the Glen

Cove unstabilized ash and other sequential batch extractions supports this finding.

Although dioxins and furans appear to be tightly bound to ash and are not readily released from ash in seawater or distilled water, it should not be concluded that they are entirely immobilized. Trace amounts may be released, which would be undetectable in both the leachate tests and block loss measurements.

The artificial reefs are visited and monitored on a regular basis by divers using SCUBA. The condition of the blocks and the inhabitants are recorded over time. Within weeks after submersion in early Spring, the entire exposed surface of the SIA and cement blocks are colonized by hydroids, polyp colonies of the class Hydrozoa. These organisms are grazed upon by the juvenile fish inhabiting the reef. This simple relationship is one example of how trace amounts of released dioxin may be of significance. If the slightest uptake occurs by the hydroids, it may be bioaccumulated within the fish over time. Fish, in turn, are eaten by other organisms including humans. Several studies have shown significant concentrations of dioxins and furans in sport and commercial fish as well as crustacea and molluscs that are eaten by humans (Batterman *et al.*, 1989; Birmingham *et al*, 1989; Fehringer *et al.*, 1984; Miyata *et al.*, 1987; O'Keefe *et al.*, 1983).

Roethel *et al.* (1990) have analyzed hydroids collected from each reef for dioxins and furans. Hepta- and octachlorinated dioxins, as well as octachlorinated furan, were detected within the hydroids obtained from the cement reef. No dioxins or furans were detected in hydroids collected from the SIA reef, however detection limits were significantly higher than those for the cement reef samples and results are inconclusive. However, the fact that the compounds were detected within the hydroids, validifies the concern pertaining to bioaccumulation. More extensive work with hydroids and other reef organisms is needed in order to assess the potential hazards of using SIA in artificial reef construction.

In deciding whether stabilized incinerator ash should or should not be used in aquatic environments, the benefits of its use must be considered as well as the potential adverse impacts. Stabilization of incineration residue would most certainly retard release of organic and inorganic contaminants and reduce the risk of environmental contamination. Underwater structures such as artificial reefs and breakwaters could be economically constructed.

Reefs support diverse communities and provide food and shelter for its inhabitants. Artificial reefs are designed to support commercial and recreational fisheries, to increase the production and diversity of colonizing organisms, and to enhance primary productivity. Reefs can also be used to mitigate losses and impacts do to development in coastal areas.

The Japanese have been manufacturing and testing stabilized fly ash structures designed specifically for reef construction, and have become the world's leader in artificial reef design, technology and utilization (Duedall and Champ, 1991). Each reef is designed for a specific purpose. They can be constructed to attract specific species, depending on shape of the structure and size of crevices. Reefs are also made to induce upwelling that stimulates primary productivity and benefits the entire area.

Artificial reefs and underwater structures should be made of economical materials that are easily available. Municipal solid waste incineration residues are not only economical but would otherwise be useless and costly due to transport and disposal. Using the residues of incineration in cementous structures is but another way of recycling, simultaneously reducing the amount of damage to terrestrial and aquatic areas being exploited for sand and gravel resources.

## Analytical Technique for the Analysis of Dioxin and Furan

One of the objectives of this study was to develop the analytical protocols necessary to detect chlorinated dioxins and furans in ash and leachate samples. The protocols used were based on those available in the current literature that have been accepted as techniques for the detection and quantitation of the compounds of concern. Although low ppb determinations were obtained, many samples in this study contained dioxins and furans at lower concentrations, as shown by the Baltimore combined ash samples analyzed by Roethel *et al.* (1990). The main difference in the protocols used was at the last step before GC/MS analysis. Final sample volume was concentrated to 100 $\mu$l as opposed to 1 ml in the present work. This final volume difference is an order of magnitude and may account for the inability to detect the compounds in the present study. When final sample volume is smaller, detection limits are lower simply due to concentrating the compounds (O'Keefe *et al.*, 1982).

## Conclusion

Since many communities are choosing incineration as their alternative to landfilling, the use of incineration residues in artificial reef construction is very appealing. This study has presented an overview of the possible fates of dioxins and furans in aquatic environments, and has provided some data suggesting that the nature of these contaminants limits their bioavailability and mobility from stabilized incineration ash.

The data from this study suggests that dioxins and furans associated with incinerator ash are not readily released from raw ash or stabilized ash into distilled water or seawater. It is hoped that this preliminary investigation of dioxin and furan mobility from stabilized incineration ash will lead to more extensive studies. A better understanding is needed of how stabilization effects the binding of these compounds to the ash. The analytical techniques must be studied further and sensitivity increased in order to detect the trace levels of dioxins and furans in these types of samples. Without a more sensitive analysis the impact of trace amounts in water and biota will not be fully understood.

# REFERENCES

Adams, W.J. and K.M. Blaine. 1986. A water solubility determination of 2,3,7,8-TCDD. **Chemosphere** 15: 1397-1400.

Agency for Toxic Substances and Disease Registry (ATSDR). **Toxicological Profile for 2,3,7,8-TCDD.** 1989. Prepared by Syracuse Research Corporation for Agency for Toxic Substances and Disease Registry. U.S. Public Health Service in collaboration with U.S. EPA.

Amdur, M.O., J. Doull, C.D. Klaassen, Eds. 1991. **Casarett and Doull's Toxicology: The Basic Science of Poisons, 4th Ed.** Pergamon Press, Inc.

Amendola, G.A. 1987. The occurrence and fate of PCDDs and PCDFs in bleached Kraft paper making processes. In: **Proceedings of the Seventh International Symposium on Chlorinated Dioxins and Related Compounds.** Las Vegas, NV: University of Nevada.

AWD Technology. 1990. Municipal waste combustion ash and leachate characterization, monofill, second year. Submitted to US EPA for publication.

Ballschmiter, K., I. Braunmiller, R. Niemczyk and M. Swerev. 1988. Reaction pathways for the formation of polychlorodibenzo-*p*-dioxins and furans in combustion processes II: chlorobenzenes and chlorophenols and precursors in the formation of polychlorodibenzo-*p*-dioxins and dibenzofurans in flame chemistry. **Chemosphere** 17: 995-1005.

Batterman, A.R., R.M. Cook, D. B. Lodge, D.B. Lothenback, B.C. Butterworth. 1989. Methodology used for a laboratory determination of relative contributions of water, sediment and food chain routes of uptake for 2,3,7,8-TCDD bioaccumulation by lake trout in Lake Ontario. **Chemosphere** 19: 451-458.

Beck, H., A. Drob, K. Eckart, W. Mathar, and R. Wittkowski. 1989. PCDDs, PCDFs, and related compounds in paper products. **Chemosphere** 19: 655-660.

Bellin, J.S. and D.G. Barnes. 1987. **Interum Procedures for Estimating Risks with Exposures to Mixtures of Chlorinated Dibenzo-*p*-dioxins and Dibenzofurans (CDDs and CDFs).** U.S. Environmental Protection Agency, EPA/625/3-87/012.

Belton, T., R. Hazan, B. Ruppel. 1985. **A Study of Dioxin (2,3,7,8-Tetrachlorodibenzo-*p*-dioxin) Contamination in Select Finfish, Crustaceans, and Sediments of New Jersey Waterways.** Trenton, NJ: New Jersey Department of Environmental Protection.

Bingham, A.G., C.J. Edmunds, B.W.L. Graham, and M.T. Jones. 1989. Determination of PCDDs and PCDFs in car exhaust. **Chemosphere** 19: 675-679.

Bopp, R.F., M.L. Gross, Huayi Tong, H.J. Simpson, S.J. Monson, B.L. Deck and F.C. Moser. 1991. A major incindent of dioxin contamination: sediments of New Jersey estuaries. **Environmental Science and Technology** 25: 951-956.

Bruggeman, W.A., A. Opperhuizen, A. Wijbenja, O. Hutzinger. 1984. **Toxicol. Environ. Chem.** 7: 173-189.

Bumb, R.R., W.B. Crummett, S.S. Cutie, J.R. Gledhill, R.H. Hummel, R.O. Kagel, L.L. Lamparski, E.V. Luoma, D.L. Miller, T.J. Nestrick, L.A. Shadoff, R.H. Stehl and J.S. Woods. 1980. Trace chemistries of fire: a source of chlorinated dioxins. **Science** 210(4468): 385-389.

Bumpus, J.A., M. Tien, D. Wright, and S.D. Aust. 1985. Oxidation of persistent environmental pollutants by a white rot fungus. **Science** 210(4706): 1434-1436.

Buser, H.R. 1979. Formation and identification of tetra- and penta-chlorinated dibenzo-*p*-dioxins from photolysis of two isomeric hexa-chlorodibenzo-*p*-dioxins. **Chemosphere** 4: 251-257.

Buser, H.R. and C. Rappe. 1984. Isomer-specific separation of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins by high-resolution gas-chromatography mass-spectrometry. **Analytical Chemistry.** 56(3): 442-448.

Chiu, C.H., M.J. Bumbaco, and R.C. Lao. 1989. Interlaboratory comparison studies on the measurement of PCDD/PCDF in pulp and paper matrices. **Chemosphere** 19: 7-12.

Clement, R.E. and H.M. Tosine. 1989. Analysis of chlorinated dibenzo-*p*-dioxins and dibenzofurans in the aquatic environment. In: Afghan, B.K. and A.S.Y. Chau, Eds. **Analysis of Trace Organics in the Aquatic Environment.** CRC Press, Inc., Florida: 151-204.

Clement, R.E., S.A. Suter, E.Reiner, D. McCurvin, and D. Hollinger. 1989. Concentrations of chlorinated dibenzo-*p*-dioxins and dibenzofurans in effluents and centrifuged particulate from Ontario pulp and paper mills. **Chemosphere** 19: 649-654.

Clement, R.E., S.A. Suter, and H.M. Tosine. 1989. Analysis of large volume water samples near chemical dump sites using the aqueous phase liquid extractor (APLE). **Chemosphere** 18: 133-140.

Crosby, D.M. and A.S. Wong. 1977. Environmental degradation of 2,3,7,8-tetrachlorodizenzo-*p*-dioxin (TCDD). **Science** 195: 1337.

Czuczwa, J.M. and R.A. Hites. 1984. Environmental fate of combustion-generated polychlorinated dioxins and furans. **Environmental Science and Technology** 18(6): 444.450.

Denison, R.A. 1988. Unpublished compilation of world-wide data and references on PCDD and PCDF in MSW incinerator ash. Environmental Defense Fund, Washington, D.C.

Dickson, L.C., D. Lenoir, O. Hutzinger, K.P. Naikwadi and F.W. Karasek. 1989. Inhibition of chlorinated dibenzo-*p*-dioxin formation on municipal incinerator fly ash by using catalyst inhibitors. **Chemosphere** 19: 1435-1445.

Duedall, I.W. and M.A. Champ. 1991. Artificial Reefs: Emerging Science and Technology. **Oceanus** 34(1): 94-101.

Eitzer, B.D. and R.A. Hites. 1988. Vapor pressures of chlorinated dioxins and dibenzofurans. **Environmental Science and Technology** 22: 1362-1364.

EPA. 1986. Method 8280. US Environmental Protection Agency. Washington, D.C.

Esposito, M.P., T.O. Tiernan and R.E. Dryden. 1980. **Dioxins.** US Environmental Protection Agency, EPA 600/2-80-197.

Fehringer, N.V., S.M. Walter, R.F. Kozara and L.F. Schneider. 1985. A survey of 2,3,7,8-TCDD in fish from the Great Lakes and selected Michigan Rivers. **Chemosphere** 14: 909-912.

Fingerhut, M.A., W.E. Halperin, D.A. Marlow, L.A. Piacitelli, P.A. Honchar, M.H. Sweeney, A.L. Greife, P.A. Dill, K.Steenbed and A.J. Suruda. 1991. Cancer mortality in workers exposed to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. **New England Jounal of Medicine** January, 24: 212-218.

Finkel, J.M., R.H. James, K.W. Baughman, J.C. Pau, J.E. Knoll, and M.R. Midgett. 1989. Efficiency of dioxin recovery from fly ash samples during extraction and clean up process. **Chemosphere** 19: 67-74.

Firestone, D., R.A. Niemann, L.R. Schneider, J.R. Gridley and D.E. Brown. 1985. Dioxin residues in fish and other foods. **Abstracts of papers of the American Chemical Society** 189: 4.

Freeman, R.A. and J.M. Schroy. 1986. Modeling the transport of 2,3,7,8-TCDD and other low volatility chemicals in soils. **Environmental Progress** 5(1): 28-33.

Gobas, F.A.P.C., K.E. Clark, W.Y. Shiu and D. Mackay. 1989. Bioconcentration of polybrominated benzenes and biphenyls and related superhydrophobic chemicals in fish: role of bioavailability and elimination into the feces. **Environmental and Toxicological Chemistry** 8: 231-241.

Gobas, F.A.P.C., E.J. McNeil, L.Lovett-Doust and G.D. Haffner. 1991. Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. **Environmental Science and Technology** 25: 924-929.

Harless, R.L., E.O. Oswald, R.G. Lewis, and A.E. Dupuy, Jr. 1982. Determination of 2,3,7,8-TCDD in fresh water fish. **Chemosphere** 11: 193-198.

Harless, R.L., E.O. Oswald, M.K. Wilkinson, A.E. Dupuy, D.D. McDaniel, and Han Tai. 1980. Sample preparation and GC-MS determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. **Analytical Chemistry** 52: 1239-1245.

Hutzinger, O. and H. Fiedler. 1989. Sources and emissions of PCDD/PCDF. **Chemosphere** 18: 23-32.

Karasek, F.W. and L.C. Dickson. Model studies of polychlorinated dibenzo-*p*-dioxin formation during municipal refuse incineration. **Science** 237: 754-756.

Karasek, F.W. and F.I. Onuska. 1982. Trace analysis of the dioxins. **Analytical Chemistry** 54: 309-324.

Karickhoff, S.W. and K.R. Morris. 1987. Pollutant sorption: relationship to bioavailability. In: **Fate and Effects of Sediment-bound Chemicals in Aquatic Systems.** K.L. Dickson, A.W. Maki, and W.A. Brungs, Eds. Pergamon Press, NY: 75-83.

Kimbrough, R.D. 1974. Polychlorinated compounds and related chemicals. **CRC Critical Review of Toxicology** 2: 445.

Kimbrough, R.D. 1990. How toxic is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin to humans? **Journal of Toxicology and Environmental Health** 30: 261-271.

Kuehl, D.W., P.M. Cook, A.R. Batterman, and B.C. Butterworth. 1987a. Isomer dependent bioavailability of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from municipal incinerator fly ash to carp. **Chemosphere** 16: 657-666.

Kuehl, D.W., P.M. Cook, A.R. Batterman, D.B. Lothenbach, and B.C. Butterworth. 1987b. Bioavailability of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from contaminated Wisconsin River sediment to carp. **Chemosphere** 16: 667-679.

Kuehl, D.W., P.M. Cook, A.R. Batterman, D.B. Lothenbach, B.C. Butterworth and D.L. Johnson. 1985. Bioavailability of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin from municipal incinerator fly ash to freshwater fish. **Chemosphere** 14: 427-437.

Lamparski, L.L, T.J. Nestrick. 1980. Determination of tetra-, hexa-, hepta-, and octachlorodibenzo-*p*-dioxin isomers in particulate samples at parts per trillion levels. **Analytical Chemistry** 52: 2045.

Mariani, G., E.Benfenati, an dR.Fanelli. 1990. Concentrations of PCDD and PCDF in different points of a modern refuse incinerator. **Chemosphere** 21: 507-517.

Marklund, S., C. Rappe, C. Tysklind and K.E. Egeback. 1987. Identification of polychlorinated dibenzofurans and dioxins in exhausts from cars run on leaded gasoline. **Chemosphere** 16: 29-36.

Marple, L., B. Berridge, and L. Throop. 1986. Measurement of the water-octanol partition coefficient of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. **Environmental Science and Technology** 20: 397-399.

Marple, L., R. Brunck and L. Throop. 1986b. Water solubility of 2,3,7,8-tetrachlorodibenzo-*p*- dioxin. **Environmental Science and Technology** 20: 180-182.

Matsumura, F., J. Quensen and G. Tsushimoto. 1983. Microbial degradation of TCDD in a model ecosystem. In: R.E. Tucker *et al.*, Eds. **Human and Environmental Risks of Chlorinated Dioxins and Related Compounds.** Plenum Press, NY: 191-219.

McCarthy, J.F. and B.D. Jiminez. 1985. Interaction between polycyclic aromatic hydrocarbons and dissolved humic material: binding and dissociation. **Environmental Science and Technology** 19: 1072-1076.

McGinnis, G.D., H.E. Ervin, B.C. Amlicke and L.L. Ingram, Jr. 1979. Analysis of low levels of pentachlorphenol and dioxins by high performance liquid chromatography. **Journal of American Wood Preservatives Association:** 233.

Mehrle, P.M., D.R. Buckler, E.E. Little, *et al.* 1988. Toxicity and bioconcentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzofuran in rainbow trout. **Environmental Toxicological Chemistry** 1: 47-62.

Meyer, C., P. O'Keefe, D. Hilker, L. Rafferty, L. Wilson, S.Connor, K. Aldous, K. Markussen, and K. Slade. 1989. A survey of 20 community water systems in New York State for PCDDs and PCDFs. **Chemosphere** 19: 21-26.

Miller, G.C., V.R. Hebert, and R.G. Zepp. 1987. Chemistry and photochemistry of low-volatility organic chemicals on environmental surfaces. **Environmental Science and Technology** 21: 1164-1167.

Miller, G.C. and R.G. Zepp. 1987. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin: environmental chemistry. In J.H. Exner, Ed. **Solving Hazardous Waste Problems: Learning from Dioxins.** American Chemical Society, Washington, D.C.: 82-95.

Miyata, H., K. Takayama, J. Ogaki, T. Kashimoto, and S. Fukushima. 1987. Monitoring of PCDDs in Osaka Bay using blue mussel. **Chemosphere** 16: 1817-1822.

Muir, D.C.G., B.E. Townsend, and G.R.B. Webster. 1985. Bioavailability of $^{14}$C-1,3,6,8-tetrachlorodibenzo-*p*-dioxin to aquatic insects in sediment and water. In L.H. Keith, C. Rappe, and G. Choudhary, Eds. **Chlorinated Dioxins and Dibenzofurans in the Total Environment II.** Butterworth Publishing, Boston: 89-101.

Muir, D.C.G. A.L. Yarechewski, and G.R.B. Webster. 1985. Bioconcentration of four chlorinated dioxins by rainbow trout and fathead minnows. In: R.C. Bahrer and D.J. Hansen, Eds. **Aquatic Toxicology and Hazard Assessment: 8th Symposium**, ASTM STP 891, American Society for Testing and Materials, Philidelphia: 440-454.

Murphy, B.L. 1989. Modeling the leaching and transport of 2,3,7,8-TCDD from incinerator ash in landfills. **Chemosphere** 19: 433-438.

Neal, H.A. and J.R. Schubel. 1987. **Solid Waste Management and the Environment**. Prentice Hall, Englewood Cliffs: 98-105.

Nestrick, T.J., L.L. Lamparski and R.H. Stehl. 1979. Synthesis and indentification of the 22 tetrachlorodibenzo-*p*-dioxin isomers by high performance liquid chromatography and gas chromatography. **Analylitcal Chemistry** 51: 2273.

North Atlantic Treaty Organization (NATO). 1988. Scientific Basis for the Development of the International Toxicity Equivalency Factor Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. **Pilot Study on International Information Exchange on Dioxins and Related Compounds, Report No. 178.** NATO, Committee on the Challenges of Modern Society.

Norwood, C.B., M. Hackett, R.J. Pruell, B.C. Butterworth, K.J. Williamson, and S.M. Naumann. 1989. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in selected estuarine sediments. **Chemosphere** 18: 553-560.

Nottrodt, A., U. Duwel, and K. Ballschmiter. 1989. Influence on formation of PCDD/PCDF in municipal solid waste plants-results of investigations at several plants in the FRG. **Chemosphere** 19: 309-316.

NUS Corporation. 1990. Municipal waste combustion ash and leachate characterization, monofill, second year. Submitted to US EPA for publication.

O'Keefe, P., D. Hilker, C. Meyer, K. Aldous, L. Shane, R. Donnelly, R. Sloan, L. Skinner, and E. Horn. 1984. Tetrachlorodibenzo-*p*-dioxins and tetrachlorodibenzofurans in Atlantic Coast Striped Bass and in selected Hudson River fish, waterfowl and sediments. **Chemosphere** 13: 849-860.

O'Keefe, P., C. Meyer, and K. Dillon. 1982. Comparison of concentration techniques for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. **Analytical Chemistry** 54: 2623-2665.

O'Keefe, P., C. Meyer, D. Hilker, K. Aldous, B.Jelu-Tyror, K. Dillon, R. Donnelly, E. Horn, and R. Sloan. 1983. Analysis of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in Great Lakes fish. **Chemosphere** 12: 325-332.

O'Keefe, P., C. Meyer, R. Smith, D. Hilker, K. Aldous, and L. Wilson. 1986. Reverse-phase adsorbent cartridge for trapping dioxins in drinking water. **Chemosphere** 15: 1127-1134.

O'Keefe, P., R.M. Smith, D.R. Hilker, W. Gilday. 1984. In: L.H. Keith, G. Choudhary and C. Rappe, Eds. **Chlorinated Dioxins and Dibenzofurans in the Total Environment II** Butterworth Press, Woburn, MA: 110-124.

Ontario Ministry of the Environment. 1985. Scientific Criteria Document No. 4-84. **Polychlorinated Dibenzo-*p*-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs).** Prepared for Intergovernmental Relations and Hazardous Contaminants Coordination Branch, Ottawa, Canada.

Palansky, J., S. Kapila, S.E. Manahan, A.F. Vonders, R.K. Malhotra and T.E. Clevenger, 1986. Studies on vapor phase transport and role of dispersing medium on mobility of 2,3,7,8-TCDD in soil. **Chemosphere** 15: 1389-1396.

Pfeiffer, C.D. 1979. Determination of chlorinated dibenzo-*p*-dioxins in pentachlorophenol by liquid chromatography. **Journal of Chromatography Science** 14: 386.

Podoll, R.T., H.M. Jaber, and T. Mill. 1986. TCDD: Rates of volatilization and photolysis in the environment. **Environmental Science and Technology** 20: 490-492.

Poland, A., E. Glover and A.S. Kende. 1976. Stereospecific high affinity binding of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin by hepatic cytosol. **Journal of Biological Chemistry** 251: 4936-4946.

Poland and Knutson. 1982. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin and related halogenated aromatic hgdrocarbons: Examination of the mechanism of toxicity. **Annual Review of Pharmacology and Toxicology** 22: 517-554.

Rappe, C. 1984. Analysis of polychlorinated dioxins and furans. All 75 PCDDs and 135 PCDFs can be identified by isomer-specific techniques. **Environmental Science and Technology** 18: 78-90.

Rappe, C., R. Andersson, P-A. Bergqvist, C. Brohede, M. Hansson, L-O Kjeller, G. Linstrom, S. Marklund, M. Nygren, S. Swanson, M. Tysklind, and K. Wiberg. 1987. Overview on environmental fate of chlorinated dioxins and dibenzofurans: sources, levels and isomeric pattern in various matrices. **Chemosphere** 16: 1603-1618.

Rappe, C., L.-O Kjeller, P. Bruckman, and K.H. Hackhe. 1988. Identification and quantitation of PCDDs and PCDFs in Urban Air. **Chemosphere** 17: 3-20.

Reggiani, G. 1981. Toxicology of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD): short review of its formation, occurrence, toxicology and kinetics, discussing human health effects, safety measures and disposal. **Regulatory Toxicology and Pharmacology** 1: 212.

Roberts, L. 1991. Dioxin risks revisited. **Science** 251: 624-626.

Roethel, F.J., V. Schaeperkoetter, R. Gregg, K. Park. 1986. The Fixation of incineration residues. Marine Sciences Research Center Working Paper No. 26, State University of New York at Stony Brook.

Roethel, F.J., V.T. Breslin, and K. Aldous. 1990. Mobility of dioxins and furans associated with stabilized incineration residues in the marine environment. In: **Proceedings of the Sixteenth Annual RREL Hazardous Waste Research Symposium.** US Environmental Protection Agency, EPA/600/9-90 037: 251-262.

Rondorf, B. 1986. Thermal properties of dioxins, furans and related compounds. **Chemosphere** 15: 1325-1332.

Ross, B.J., K.P. Naikwadi, and F.W. Karasek. 1989. Effect of temperature, carrier gas and precursor structure on PCDD and PCDF formed from precursors by catalytic activity of MSW incinerator fly ash. **Chemosphere** 19: 291-298.

Ryan, J.J., P.Y. Lau, Pilon, *et al.* 1984. Incidence and levels of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in Lake Ontario commercial fish. **Environmental Science and Technology** 18: 719-721.

Sawell, S.E. and T.W. Constable. 1988a. The National Incinerator Testing and Evaluation Program Phase IIB: Assessment of contamination leachability from the residues of a mass burning incinerator. Environment Canada.

Sawell, S.E. and T.W. Constable. 1988b. The National Incinerator Testing and Evaluation Program: Characterization of Residues from a Mass Burning Incinerator. In: **Proceedings of the Tenth Canadian Waste Management Conference.**

Sawell, S.E., T.W. Constable and R.Klicius. 1989. Evaluation of contaminant leachability from residues collected at a refuse derived fuel municipal waste combustion facility. Environment Canada.

Schroy, J.M., F.D. Hileman, and S.C. Cheng. 1985. Physical/Chemical properties of 2,3,7,8-TCDD. **Chemosphere** 14:877-880.

Servos, M.R., D.C.G. Muir, D.M. Whittle, D.B. Sergeant, and G.R.B. Webster. 1989. Bioavailability of octachlorinated dioxin in aquatic ecosystems. **Chemosphere** 19: 969-972.

Shiu, W.Y., W. Doucette, F. Gobas, A. Andren, and D. Mackay. 1988. Physical-chemical properties of chlorinated dibenzo-*p*-dioxins. **Environmental Science and Technology** 22: 651-658.

Smith, L.M., D.L. Stalling, and J.L. Johnson. 1984. Determination of part-per-trillion levels of polychlorinated dibenzofurans and dioxins in environmental samples. **Analytical Chemistry** 56: 1830-1842.

Stalling, D.L., P.H. Peterman, L.M. Smith, R.J. Norstrom and M. Simon. 1986. Use of pattern recognition in the evaluation of PCDD and PCDF residue data from GC/MS analysis. **Chemosphere** 15: 1435-1443.

Stanley, J.S., T.M. Sack, Y. Tondeur and W.F. Beckert. 1988. Evaluation of a high-resolution gas chromatography/ high-resolution mass spectrometry method for the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin in soil and water. **Biomedical and Environmental Mass Spectrometry** 17: 27-35.

Steisel, N., R. Morris, and M.J. Clarke. 1987. The impact of the dioxin issue on resource recovery in the U.S. **Waste Management Resources** 5: 381-394.

Stieglitz, L. and H. Vogg. 1986. On formation conditions of PCDD/PCDF in fly ash from municipal waste incinertors. In: **Sixth International Symposium on Chlorinated Dioxins and Related Compounds**, Japan.

Tiernan, T.O., D.J. Wagel, G.F. Vanness, J.H. Garrett, J.G. Solch, L.A. Harden. 1989. PCDD/PCDF in the ambient air of a metropolitan area in the U.S. **Chemosphere** 19: 541-546.

Tong, H.Y. and F.W. Karasek. 1986. Comparison of quantitation of polychlorinated dibenzodioxins and polychlorinated dibenzofurans in complex environmental samples by high resolution gas chromatography with flame ionization, electron capture and mass spectrometric detection. **Chemosphere** 15: 1141-1146.

Tschirley, F.H. 1986. Dioxin. **Scientific American** 254: 29-35.

Tsushimoto, G., F. Matsumura and R. Sago. 1982. Fate of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) in an outdoor pond and in model aquatic ecosystems. **Environmental Toxicology and Chemistry** 1: 61-68.

Vogg, H. and L. Stieglitz. 1986. Thermal behavior of PCDD/PCDF in fly ash from municipal incinerators. **Chemosphere** 15: 1373.

Wagel, D., T.O. Tiernan, M.C. Taylor, B. Ramalingam, J.H. Garrett and J.G. Solch. 1983. Development of high performance liquid chromatography methods for separation and automated collection of tetrachlorinated dibenzo-*p*-dioxin isomers. In: Rappe, C., G. Choudhary, L.H. Keith, Eds. **Chlorinated Dioxins and Dibenzofurans in Perspective.** Lewis Publishers, Inc.: 305-327.

Walters, R.W., S.A. Ostazeski, and A. Guiseppi-Ellie. 1989. Sorption of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin from water by surface soils. **Environmental Science and Technology** 23: 480-484.

Webster, G.R.B., D.H. Muldrew, F.F. Graham, L.P. Sarna, and D.C.G. Muir. 1986. Dissolved orgainc matter mediated aquatic transport of chlorinated dioxins. **Chemosphere** 15: 1379-1386.

World Health Organization (WHO). **Polychlorinated dibenzo-*p*-dioxins and dibenzofurans.** 1989. Environmental Health Criteria 88.